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Chemical Treatment Approaches For Industrial Plant Decontamination: Mercury remedation

Liu, Yu

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CHEMICAL TREATMENT APPROACHES FOR INDUSTRIAL PLANT DECONTAMINATION

Mercury remediation

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Queen's University Belfast

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Supervisors: Prof. Martin Atkins, Dr. John Holbrey

Author: Yu Liu

Abstract

Mercury causes many problems in the processing of hydrocarbons in oil and gas industries. It is a toxic metal and can lead to disastrous failure of processing plants leading to explosions and loss of life. With many of the hydrocarbon processing plants now approaching 30 years in operation they are coming to the end of their economic life and need to be decontaminated as part of their decommissioning process. Here the problem is that mercury can “hide” inside pipelines and flanges, increasing the difficulty of plants decommissioning and recycle. Economical and applicable chemical decontamination i.e. dissolution of elemental Hg should be studied to eliminate this problem to avoid mercury exposure to worker and environment.

In this study, wet-based chemical approaches using KI/I_2 solutions were studied for the recovery of mercury as part of plant cleaning and decommissioning. The influence of solution concentration, molar ratio of $KI:I_2$, pH, temperature was investigated in this experiment. To see whether KI can be substituted by other halide salts i.e. NaBr, KBr, NaCl, KCl, mixed oxidative trihalide solutions were studied to learn its efficiency of mercury dissolution. After oxidation/dissolution of Hg^0 to Hg^{2+}, the obtained mercury(II)-containing solution need a further treatment to concentrate and capture mercury from aqueous solutions via commercial 2,4,6-Trimercapto-s-triazine, trisodium salt (TMT-15) or Purolite S924/S920 ion exchange resin, thus ensuring no mercury is left in wastewater. The operating variables of dosage, initial mercury concentration, contact time, pH and temperature were studied.

Results indicated that KI/I_2 solution was efficient on mercury dissolution, 100 mg elemental mercury could be completely dissolved in 10 ml of 4% (0.053/0.16 M I_2/KI) w/v KI/I_2 solution in 10 h at room temperature, mercury concentration was achieved of 0.050±0.002 mol/l. For bromide/iodine solution, a mercury concentration of 0.051±0.001 mol/L and 0.051±0.001 mol/L was achieved by 10 ml 0.0504/0.6531 M $NaBr/I_2$ and 0.0510/0.5630 M KBr/I_2 solution, respectively. Dissolved mercury ions were effectively removed from the aqueous solutions using S924 and S920 resin or TMT-15, producing solutions that had very low mercury contents ([Hg] ~ 0.02 g/L). A dosage of 30% molar excess (0.7 g) of TMT-15 can reduce 10 g/L mercury to 0.028±0.025 g/L with a contact time of 1 h. The resins S924 and S920 showed good removal of mercury after 4~6 h contacting, with an extraction efficiency of 84.28±0.71% and 99.16±1.91% respectively.

Key words: Mercury, potassium iodide, iodine, bromide, TMT-15, resin, Purolite S924/S920

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Abbreviations

$BDET^{2-}$	1,3-benzendiamidoethanethiol
$BDTH_2$	N,N′-bis(2-mercaptoethyl)isophthalamide
Br^-/I_2	Bromide and iodine solution
C_e	Equilibrium concentration
C_i	Initial concentration
Cl^-/I_2	Chloride and iodine solution
DMA-80	Milestone direct mercury analyser
Ea	Activation energy
EPA	The United States Environmental Protection Agency
FAO	Food and Agriculture Organization of the United Nations
g/L	Grams per liter
Hg-TMT	Chelate compounds after coordination of Hg and TMT
[Hg]	Concentration of dissolved mercury (II)
Hg^0, Hg(0)	Metallic mercury
Hg^{2+}, Hg(II)	Mercuric
IPIECA	The International Petroleum Industry Environmental Conservation Association
K_1	The adsorption rate constant of pseudo-first-order
K_2	The adsorption rate constant of pseudo-second-order
Kc	Equilibrium constant
KI/I_2	Potassium iodide and iodine solution
KJ/mol	Kilojoule per mole
km	Kilometer
L/min	Liter per minute
LME	Liquid Embrittlement
M, mol/L	Moles per liter
mg/g	Milligrams per gram

mg/kg	Milligram per kilogram
mg/kg	Microgram per kilogram
mg/L	Milligram per liter
ml	Milliliter
mmol	Millimole
ng	Nanogram
ppb	Parts per billion
ppm	Parts per million
Q_e	Adsorption capacity
Q_{max}	Maximum adsorption capacity
R^2	The corresponding coefficient
rpm	Revolution per minute
S/S	Stabilization and solidification
STC	Potassium/sodium thiocarbonate
STDC	Sodium dimethyldithiocarbamate
TMT	2,4,6-Trimercapto-s-triazine, tri-sodium salt
UNEP	The United Nations Environment Programme
w/v	Weight per volume
WHO	World Health Organization
µL	Microliter

Project objectives and experimental plan

The aim of this project is to explore low impact approaches to mercury remediation and removal from contaminated pipework and associated equipment of petroleum refineries and oil/gas terminals, this decontamination procedure could allow recycling and recovery of waste plant equipment.

In this project, the use of inorganic aqueous trihalide solutions as oxidants for mercury were explored, for the transformation of elemental mercury into water soluble halomercurate(II) species. Following this, recovery of mercury from the aqueous solutions, so that they are decontaminated for disposal, by capture or extraction from aqueous solution using commercial TMT or sulfur-containing resins was investigated to ensure no mercury was left in the wastewater.

The main stages of the study are:

1. Investigation of elemental mercury dissolution in potassium iodide/iodine solutions. The influence of solution concentration, the molar ratio of KI/I_2, contact time and temperature were examined.

2. System modification to examine the applicability of other halide salt/iodine solutions was made, testing the effectiveness of bromide and chloride solutions of iodine on dissolution of mercury.

3. Decontamination of the aqueous extraction solution, to enable safe disposal and concentration of extracted mercury, was tested using commercial reagents: trimercaptotriazine-15 (TMT-15), and Purolite S924 and S920 ion exchange resins. The influence of initial mercury concentration, solution pH, dosage, contact time and temperature on the mercury removal performance are considered.

Chapter 1

Introduction

1.1 Background

Mercury is a highly toxic heavy metal which poses a high threat to the environment. Mercury release is a global problem, it would form a mercury cycle transporting and dispersing mercury between the atmosphere, aquatic contents and sediments with different mercury forms leading to serious pollution problem. The United Nations Environment Programme (UNEP) estimated that the average mercury concentration in the Earth's crust in 2002 was 0.05 mg/kg [1]. Emission of mercury to the biosphere are caused by both natural and anthropogenic activities. Volcanic eruption, geothermal release, weathering and volatilization from ocean surface are the main reason of mercury release by natural activities. As shown in Fig. 1-1, the main source of mercury release by nature is through volatilization, which account for about 71% of the contribution of mercury emission to the atmosphere [2]. For human activities, UNEP recently estimated that gold mining and coal burning accounted for the largest proportion to mercury emissions. Fig.1-2 illustrated that small-scale gold production performed the largest contribution to the mercury emission of anthropogenic activities, and the estimated mercury release caused by oil and gas industries is about 1% of total anthropogenic emissions [1].

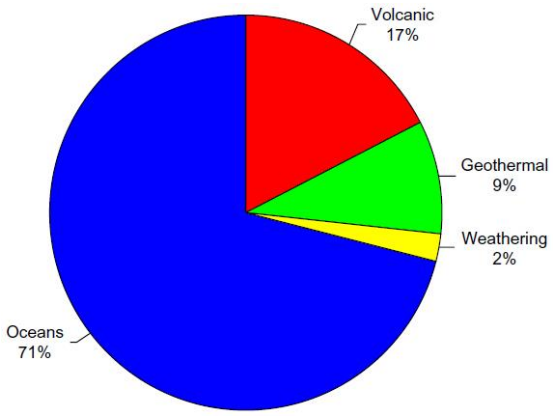


Figure 1-1 Relative contributions of estimated mercury emissions to the environment caused by natural activities [2].

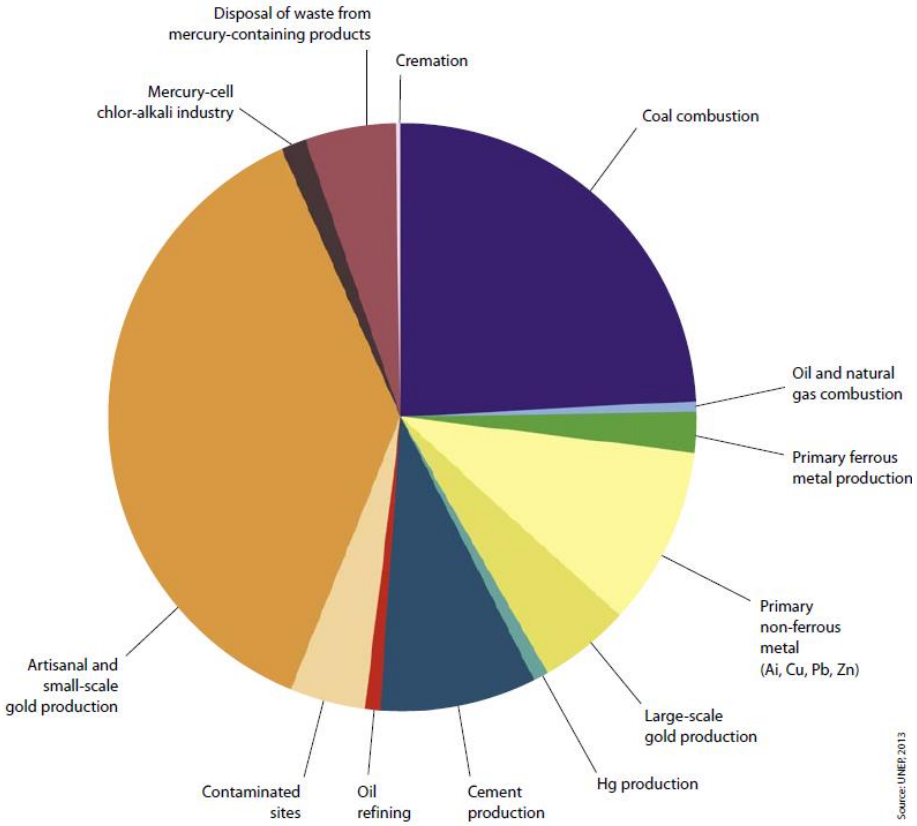


Figure 1-2 Relative contributions of estimated mercury emissions to the environment caused by anthropogenic activities [1].

In industry, there are many potential sources of mercury pollution that include coal combustion, gold mining, natural gas, oil refining, battery, fluorescent lamp manufacturing and so on. It was reported the annual emission of mercury was approximately 7527 tons in 2008, while 31% (2320 tons) among them was caused by anthropogenic activities [3]. The extraction of gold from ore materials achieved by amalgamation with elemental mercury, Reichelt et al. [4] estimated that producing one gram of Au requires 20 g of mercury, gold is concentrated by burning Hg-Au amalgam and then mercury is emitted into the air, leading to an health threat to workers and environment. Antoszczyszyn et al. [3] reviewed the literature on mercury contamination in bituminous coal and estimated a mercury content range from 30 to 300 ppb in bituminous coal. The recovery of fluorescent lamps is hard due to the

presence of toxic mercury, the total contents of mercury in these lamps are approximately 1.6 to 27 mg/lamp [5]. Mercury is also present in oil and gas, as a result of geological migration of mercury through strata and preferential solubility in hydrocarbons, the concentration of mercury depends on geographical location and on the age of the oil or gas reserves. Levels of mercury vary from approximately 0.01 ppb to 10 ppm (wt) [6]. Crude oil derived from Asia has a much higher level of mercury concentration compared to it in other regions, the concentration of mercury in crude oil derived from Asia was about 220.1μg/kg, while mercury concentration in crude oil are 2.7 μg/kg, 8.7 μg/kg, 0.8 μg/kg, 5.3 μg/kg, 3.2 μg/kg in Africa, Europe, Middle East, South America and North America, respectively [7]. A major source of mercury release to atmosphere is the combustion of hydrocarbons, it is evaluated that approximately 11 tons of mercury are emitted to the atmosphere from burning oil every year [6].

Mercury in oil and gas has a negative influence not only on the environment but also on petroleum process. Mercury presents in gas, oil, condensates and produced waters from the oil and gas extraction industries. Usually mercury accumulates through condensation, precipitation and amalgamation with different chemical forms. Mercury is a toxic metal and in hydrocarbon processing has a devastating impact on aluminum heat exchangers due to the formation of amalgams. Besides, mercury could result in a condition named Liquid Embrittlement (LME), which lead to some severe damages to large plants [8]. What's more, the presence of mercury in feedstock can cause subsequent problems with some hydrogenation catalyst poisoning further downfield in the processing chain. During the hydrocarbon processing, the present of mercury increase risk to the health and safety of workers. With many existing hydrocarbon processing plants now approaching 30 years in operation they are coming to the end of their economic life and need to be decommissioned. The main problem is that mercury can "hide" in pipelines and

flanges, the presence of mercury increasing the difficulty of plants decommissioning and recycle. For example, at one site in Thailand, an end-of-life pipeline the needs decommissioning and is mercury contaminated covers a distance of 20 to 50 km. Obviously, it's a severe contamination of mercury in this field, therefore, mercury control and decontamination should be conducted firstly during the decommissioning of oil and gas plants and terminals to make sure all the workers and contactors are not exposed during their work. In addition, equipment should be ensured that has no mercury to allow its reuse or recycle without releasing mercury to the environment. The research project is focused on establishing whether non-acidic mercury leaching as a chemical treatment solution for mercury decontamination can be contained with precipitation/adsorption of water soluble mercury species using commercial mercury scrubbing agents allow safe disposal of the bulk decontamination water solutions.

1.2 Forms of mercury

Mercury occurs in earth with various forms and different concentrations, most of its compounds and salts pose a serious risk to environment and people. Mercury occurs as inorganic and organic forms with three oxidation states: metallic (Hg^0), mercurous (Hg_2^{2+}) and mercuric (Hg^{2+}). Knowing the properties and transformations of these mercury compounds speciation is important, because it can bring some implications in identifying exposure risks, and in selecting mercury removal systems and methods. A brief review of mercury and its different compounds are showed below.

1.2.1 Elemental mercury

Elemental mercury is a silver-colored liquid substance. In atmosphere, the most forms of mercury is elemental mercury, it states mostly gaseous rather than liquid [9].

Mercury is defined as heavy metal but elemental mercury has some different

properties than other heavy metals. For example, it is a liquid at room temperature. In addition, unlike most metals, the vapor pressure of mercury can be measured at a room temperature, table 1-1 presents that vapor pressure of elemental mercury is dependent on temperature. The most volatile form of mercury is elemental mercury, it would transform into the vapor phase at a room temperature. Although it has higher vapor pressure than other heavy metals, the vapor pressure of elemental mercury is mostly lower than other liquids. For example, the vapor pressure of liquid water at 25 °C is about 3.169 $x10^3$ pa [10], which is much higher than the vapor pressure of elemental mercury. Studies show that droplet of mercury is not easy to evaporate in laboratory [1].

Table 1- 1 Vapour pressure of elemental mercury [1]

Temperature		Vapour pressure	
°C	°F	Pa	psi
0°	32°	0.027	0.00004
20°	68°	0.17	0.0002
40°	104°	0.86	0.001
60°	140°	3.5	0.005

Elemental mercury is soluble in liquid aliphatic hydrocarbons, its solubility in hydrocarbon (1-3 ppm) is higher than it (0.05 ppm) in water [6]. Although elemental mercury has very low solubility in water, various metals can be dissolved in elemental mercury to form amalgams. Katrinak et al. [11] summarized that metals such as silver, copper, zinc, gold and aluminium are available in the formation of amalgams with liquid or gaseous elemental mercury at ambient conditions. Generally, the solubility of zinc in mercury is higher than other metals. For example, 2.15 g zinc can be dissolved in 100 g mercury, however the solubility of gold in elemental mercury is 0.13 g/100 g of mercury, which is even higher than the solubility of silver, copper and aluminium in mercury [11]. Even so, the solubility is strong enough for small amounts of elemental mercury to lead to corrosion and embrittlement of steel, aluminium and copper alloy

valves and pipes. Elemental mercury is easily adsorbed on the metal surfaces and then leads to corrosion on pipe or equipment walls by reacting with iron oxides during the petroleum processing [7].

1.2.2 Mercuric sulphide

Due to the strong affinity between mercury and sulphur, mercuric sulphide accounts for the dominant proportion in the forms of mercury. It occurs as a heavy solid or amorphous powder at room temperature. Fisher [12] reported that the shape of mercuric sulphide solid could be black cubic crystals or a powder, be lumps or hexagonal. Due to its very low solubility in water and hydrocarbon, mercuric sulphide has less toxicity than other forms of mercury, so it can be used to make jewellery or ornamental. However, mercuric sulphide is easy to decompose into elemental mercury when it heated at very high temperature.

1.2.3 Mercuric chloride

Pure mercuric chloride exists as a white crystalline solid or powder. It can soluble in water, with a high solubility of 74 g/L at 20 ºC. Its solubility depends on temperature, for example, increases to 476 g/L in boiling water. It is also soluble in hydrocarbons and in many organic solvents, for example the solubility of $HgCl_2$ in ethanol 263 g/L [12]. Mercuric chloride has been shown to be unstable in refineries, because it can react with sulfur, such as mercaptans and hydrogen sulfide, which are common components in oil and gas refinery procedures.

1.2.4 Mercury oxide

Mercury oxide is a basic oxide. Its chemical formula is HgO. It occurs as red or orange solid at room temperature. The red colour mercury oxide is made by heating mercury in oxygen at 350 °C or by decomposition of mercury nitrate. The orange form is made

by the reaction between solution containing Hg^{2+} and alkali precipitation. Because mercury oxide can decompose easily, sometimes it can be used to produce mercury with the release of oxygen. Mercury oxide decomposes when it is exposed to light or is heated above 500 °C [13].

1.2.5 Mercury iodide

The molecular formula of mercury(II) iodide is HgI_2. It is hardly soluble in water, its solubility is 0.006 g/100 ml [14]. It is soluble in some hydrocarbons such as methanol, ethanol. There are two variants of mercuric iodide, one is red alpha crystalline form, tetragonal crystals, the relative density of 6.36 g/cm³ (25 °C). When temperature is above 126 °C, the red colour crystal transfers to another form of yellow beta crystal, and it turns red again when the sample is cooled. The relative density of yellow mercury iodide is 6.094 g/cm³ (127 °C). The melting point of mercury(II) iodide is 259 °C and its boiling point is 354 °C.

1.2.6 Organic mercury

Organic mercury has a high solubility in crude oil and gas condensate. Light organic mercury is considered as the most toxic compounds among the several forms of mercury. Many relative papers showed the reason why the organic mercury is so toxic, generally is due to the high ability of dissolving in or bonding with cell membranes or tissues, this ability of light organic mercury could pose a high threat to aquatic life and human health.

The most common form of light organic mercury is methylmercury, which is a volatile liquid phase and is soluble in both water and hydrocarbons. Compounds such as methylmercury or dimethyl mercury can be produced by the organic processes inside aquatic life, such as fish or algae. That’s a reason why it is necessary for researchers to decrease the emissions of mercury into the biosphere. The United States [15] have

made a survey that the predominate way for the general population to absorb organic mercury especially methylmercury is the consumption of fish and seafood. The content of organic mercury inside fish or other seafood should be controlled, in case of mercury poisoning when human eating them.

Table 1- 2 The properties of mercury and its compounds [11, 16]

Properties	Hg^0	HgS	$HgCl_2$	HgO	CH_3HgOH	$Hg(OH)_2$
Melting point (℃)	-38.8	584	277	500	137	-
Water solubility (g/L)	$49.6x10^{-6}$ (20 ℃)	$2x10^{-24}$ (25 ℃)	74 (20 ℃)	0.053 (25 ℃)	-	32.3 (25 ℃)
Boiling point (℃)	356.7	-	303	-	-	-
Vapor tension (Pa)	0.18	-	0.009	$9.2x10^{-12}$	0.9	-

1.3 Mercury contamination

In recent decades, the phenomenon of the increasing of mercury pollution at a global scale had become more and more apparent. Mercury contamination at soil, atmosphere, oceans and lakes poses a high risk to ecological environment and human health by influencing the food chain. According to the contaminated sites, mercury contamination could be divided into three main categories: soil, water and air. Before carry out a mercury remediation method, type of mercury contamination should be defined. To identify the extent of mercury contamination into the soil or water, it's important to consider the surrounding environment of the given sites and its geophysical and hydrogeological structure, it also help in estimating the most suitable type of remediation and management [17]. A literature review of mercury contamination and remediation are showed below.

1.3.1 Mercury contamination in soil/solid

Natural activities such as rocks weathering or volcanic eruption, could cause mercury pollution in soil. Anthropogenic activities include gold mining, coal burning, cement production, metal refining, mercury production or other activities could release a great

amount of mercury into the environment or soil. The data shows that the average concentration of mercury in soil caused by natural activities is about 0.06 mg per kg of soil, and the recent global yearly emission of mercury is estimated within a range from 5000 to 8000 metric tons [18].

Some organic compounds or bacteria inside soil can react with this environmentally generated mercury and produce more toxic organic mercury compounds such as methylmercury through biotic reactions. What's more, the obligate anaerobic sulphate-reducing bacteria could mediate the biotic reaction. Methylmercury is so toxic that it can cause wide spread soil contamination and pose a risk to human health. Specific hazards of mercury in soil can include: mercury could be absorbed by plants and crops and then accumulated into human or other animals' body through food chain. Mercury pollution on food crops plays a main role in threatening human health. Qian et al. [19] reported that vegetables grown in contaminated soil with mercury contents in the range from 0.09 to 0.54 mg/kg had an average mercury concentration of 0.09 mg/kg. People should think highly of the mercury concentration inside contaminated vegetables because GB 2762-2005 (China Food Safety National Standard for maximum levels of contaminants in foods) made a standard that the mercury limitation inside vegetables and fruits is about 0.01 mg/kg. What's more, Food and Agriculture Organization of the United Nations (FAO) and World Health Organization (WHO) reported that the tolerable weekly tolerable intake of mercury is 0.3 mg and methylmercury should less than 0.2 mg [20]. Only when mercury concentration in foods is less than these levels can hazards to human health be minimised.

Anthropogenic activities such as gold mining activities, chlor-alkali plants, production of non-ferrous metals, landfill of mercury-containing waste and some other industrial processes could lead to a rising of mercury concentration in soil. For mercury mining, the ways of mercury release into environment or soil are primary inefficient retorting

and erosion of mine wastes. Bailey et al. [21] investigated an abandoned mercury mines located in south-western Alaska and found the mercury concentration in soil are 0.05 to 5326 mg/kg. For the gold mine, small-scale gold mining has a risk to environment because mercury would be used in the extraction of gold. Mercury is added to form an amalgam with gold after grinding the gold ore. Heat the amalgam and then gold will be concentrated as a pellet but elemental mercury would be emitted into the environment or soil. Feng et al. [22] reported that the soil samples of gold mining in Tongguan, China have a total mercury concentration within a range from 0.9 to 76 mg/kg. Pataranawat [23] found mercury concentration in soil of a small-scale gold mining located in Pichchit, Thailand was about 10.5 mg/kg. Soils around some production industries of chemicals have a high mercury concentration because the use of mercury, for example, mercury is used as a liquid cathode during the production of chlorine and soda, soil contamination caused by the discharge of mercury-containing wastewater to land. Bernaus et al. [24] reported a high mercury content of 1139 mg/kg in soils near a chlor-alkali factory in Netherlands. Grangeon [25] estimated a mercury concentration of 0.07 to 2.51 mg/kg in soils, which were sampled from surrounding land of a mercury cell chlor-alkali factory in Grenoble, south-east France. Landfill accounts for a large part of soil contamination, mercury-containing waste such as discarder thermometers, blood-pressure meters, batteries and fluorescent lamps can increase the concentration of mercury in soil when they are deposited in landfill, the mercury pollution of these waste deposited in landfill account for about 40% of the Hg discharge in North America [26]. Earle et al. [27] investigated a solid waste landfill located in Florida, USA, and the mercury concentration in that waste was at a range of 0.03 to 16.8 mg/kg with a geometric mean of 0.18 mg/kg. Chai et al. [28] analyzed a management of methylmercury in landfill located in Shanghai and reported the average concentration of mercury was about 0.27 mg/kg.

1.3.2 Mercury contamination in air

Mercury emission sources to air include both natural and anthropogenic sources. It is reported that there have about 5000-7000 tons of mercury are emitted to atmosphere from all its sources every year [29, 30]. The ratio of mercury emission caused by natural and anthropogenic is not determined accurately but generally has a range of 0.8 to 1.8 [29]. The large amount of mercury emission in atmosphere are caused by the instability and low volatility of mercury compounds and various sources, mercury exists almost in the gas phase as elemental mercury and methylmercury in the atmosphere, inorganic mercury compounds occur in atmosphere as particle-associated condition. Aquatic system such as ocean, lake and river can release mercury to atmosphere through evaporation. It was investigated that 60% of mercury emissions to air are caused by surface waters from Indian, Pacific and Atlantic oceans, mercury emission caused by a re-emission from soil in tropical and subtropical presents about 40%, mercury emission from snow melting account for 8% and volcanoes presents 2% [31].

Processes that use mercury directly as a raw material or catalyst including gold mining, chlor-alkali production, control and measurement equipment and where mercury is an impurity in raw materials including energy generation processes, non-ferrous metals production and cement production are the main source of mercury emission to atmosphere caused by human activities. Wilson et al. [32] divided the global mercury release into air from human activities into several parts in 2002: coal combustion and small-scale gold mining represents the largest proportion, which is 27.9% (116.1-820.7 mg/kg) and 32% (409.7-906.2 mg/kg) respectively. Mercury emission from burning of petroleum derivatives and natural gas has a range of 4.3 to 15.3 mg/kg, represent 0.4%. 10.8% (79.5-431.6 mg/kg) of mercury release into air are caused by cement. Gas-phase mercury can be emitted into air from coal-fired power, Wang et al. [33] estimated the average mercury content in coal of China was about

0.19 mg/kg and the total Hg emission to air by the whole coal power industries in China was about 292 tons in 2004.

1.3.3 Mercury contamination in water

Mercury contamination could not only present in soil and air but also in aquatic system. Since some forms of mercury such as elemental mercury and methylmercury are easily evaporable into atmosphere, the main source of mercury contamination in water is from rain, snow and other atmospheric deposition. Some anthropogenic activities including coal combustion, metal mining, oil refining could release mercury-containing industrial effluent into rivers, lakes and oceans.

Mercury pollution pose a high risk to aquatic life. The exact mechanism of how mercury enters the food chain is still under study. However, nobody can deny that the bacteria in aquatic ecosystem play an important role to transform inorganic mercury into methylmercury, which is much more toxic than inorganic mercury. It requires a longer time for organisms to estimate methylmercury than other inorganic mercury, so organisms can accumulate methylmercury easier inside their body and the methylmercury-containing bacteria would be consumed by the higher level organisms in the food chain, or the methyl mercury may be released by bacteria or algae to water and then absorb by some planktons, which could be consumed by the higher level organisms as well [34]. Therefore, mercury pollution in aquatic ecosystem pose a high risk to human health because human is the top level in the food chain and the way of mercury uptake inside human body could through the consumption of fishes and seafood.

Mercury has various pathways through the environment. Figure 1-3 illustrates the cycling pathway of mercury in aquatic environment. It indicates that the main source of mercury release into the aquatic ecosystem is from the deposition from atmosphere, primarily from rainfalls. Once the deposition of atmosphere enters the water, could

mercury compounds transform into another form of mercury by the biochemical reaction. Both inorganic mercury (II) and methylmercury could be absorbed by sediment accumulated in the bottom and then be released to water through diffusion. Toxic mercury compounds may be bio-accumulated in the body of aquatic life and enter the food chain, it would also release back to atmosphere through volatilization and then complete a full cycle.

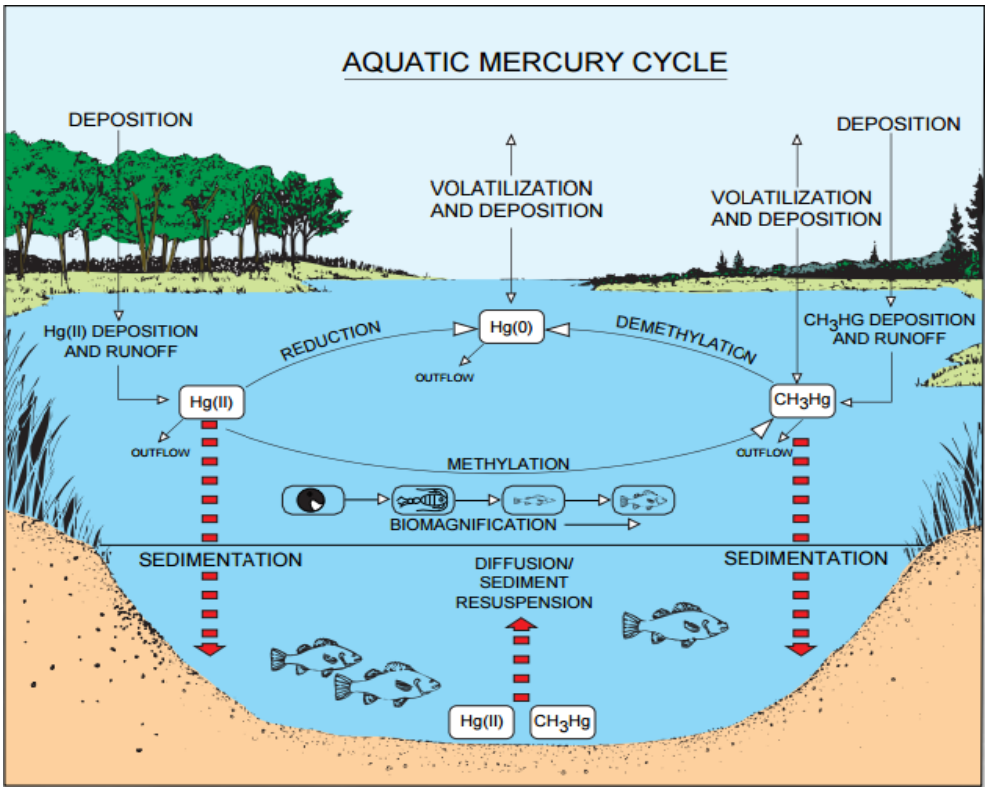


Figure 1-3 Mercury cycle in aquatic system [34]

1.3.4 Mercury contamination in oil refining

Although the global emission of mercury caused by crude oil only account for about 1-2%, it still has about 238 kg and 140 kg of mercury released from petrol and diesel oil respectively [35]. Mercury can be discharged to soil, water and atmosphere by oil and gas industries through waste, effluent and combustion. In oil and gas refineries and offshore installations, deposits or sludge of liquid elemental mercury can be found

in refining equipment and crude oil piping. During the process of oil refining, mercury could be deposited on the internal surface of equipment or plants. For example, mercury would deposit on the metal surface of petroleum pipelines when the mercury-laden oil transit through. The presence of mercury has a potential hazard of contamination to oil& gas refining and transport metal equipment. Metals such as steel and aluminium would be vulnerable to cracking if it contacted with mercury for a long time. In the petroleum industry, process equipment degradation includes LME, stress cracking and aluminium corrosion and oxidation. Liquid metal embrittlement is a phenomenon that specific metals loss its tensile ductility and result in a sudden cracking when it exposed to a molten or liquid metal [36]. Elemental mercury is a liquid metal at temperature above -38 ºC and could form an amalgam resulting in brittle cracking when it contacts with some alloying systems, especially with aluminium and copper. As the human and industrial demand of oil is increasing, there have more mercury that exists in crude oil process through the oil refining systems. That means there will have more alloy equipment suffer from the damage of LME. In order to protect the integrity of oil refining or transport plants and to ensure these plants could be reused or recycled without mercury, engineers should choose materials of equipment that is not easy to be influenced by LME caused by mercury.

The International Petroleum Industry Environmental Conservation Association (IPIECA) reported some areas where mercury could exist in a refinery. Here give some examples [1]: decommissioned process equipment and pipelines; crude oil distillation unit; sludge in tank bottom; waste polymerization catalysts; sludge and sediment in wastewater treatment plants. For the purpose of protecting workers from exposure of mercury, measures including control the amount of mercury intake in crude oil, worker personal protection, safe design of plants and ventilation should be conducted. Additionally, equipment should be often flushed in order to clean the mercury-containing sediment or sludge deposit inside these facilities. If necessary, decontamination and remediation of equipment should be done in case the exposure

of mercury.

1.4 Mercury remediation

Due to the toxicity, mercury has many hazards no matter how it is emitted to the environment or deposited in oil and gas refining and transport equipment. There have many ways for worker exposed to mercury during their daily work hours, including inhalation, ingestion and contact with eyes and skin. Depending on the toxicity of different forms of mercury and on exposure duration, there have different toxic effects. WHO [1] reported that harmful phenomenon such as lung damage, blood pressure and heart rate increases, nausea, diarrhoea would be caused by high short-term mercury exposures. It's important and necessary to remove mercury and prevent mercury contamination in order to protect our environment and give a guarantee for human health. As mentioned, mercury contamination could in occur soil, air and water. Paper reported that the "soil waste" includes land or soil, sediments, sludge and some other solid-phase environment waste generated by industry; "water" contains drinking water, groundwater and wastewater released by industries [37]. Due to various kinds of mercury contamination and different backgrounds of pollution such as gold mining, oil refinery and transport, coal combustion and so on, different methods of remediation should be considered and compared. There have three specific points need to be taken into account when proposing a remediation strategy of mercury contamination [37]:

(1) Firstly, it should make sure an accurate conceptual model which includes a detailed survey of mercury contaminated sites and estimation on the potential transformation and pollution degree of mercury during the remediation treatment. That means researchers and engineers should design or improve a detailed optimal remediation method according to the characterization of mercury exist in various environmental compartments and the transformation of various mercury forms.

Besides, all the remediation techniques used should be efficient in preventing human health and environment from the contamination of mercury. The final mercury concentration of waste should be controlled and below a standard value.

(2) The mercury waste remained by mercury remediation produces should be properly conducted because mercury can't be destroyed. The cost used in the final wastes dispose need to consider the volume and weight of wastes. It's necessary to control the cost in a remediation project. With the close efficiency of removing mercury, the cheaper method is more likely to be selected. Before going to disposal, the stability of waste should be considered and improved.

(3) During the remediation project implementation, due to the low vapour pressure, mercury can be circulated through rainfall and runoff processes in air. So it's necessary to protect surrounding environment and the safety of workers during the decontaminated works. Table 1-3 presents some limit values of mercury exposure provided by some countries authoritative institutions. For UK, the amount of mercury compounds should be no more than 0.02 mg per m^3 workplace. Companies, industries and laboratories should obey the requirement in their nation or region in order to protect human's health.

Table 1-3 Mercury limit in different countries and regions [1]

UK WEL (Workplace Exposure Limits)	DFG MAK (German Research Foundation)	The Netherlands	US ACGIH (American Conference of Governmental Industrial Hygienists)	US OSHA (Occupational Safety and Health Administration
Elemental and inorganic mercury 0.02 mg/m^3 (8 hours)	Elemental and inorganic mercury 0.02 mg/m^3 (8 hours)	Elemental and inorganic mercury 0.02 mg/m^3 (8 hours)	Elemental and inorganic mercury 0.025 mg/m^3 (8 hours)	Elemental and inorganic mercury 0.1 mg/m^3 (8 hours)
		Alkyl mercury 1.1 mg/m^3 (8 hours) 1.2 mg/m^3 (15 minutes)	Alkyl mercury 0.01 mg/m^3 (8 hours) 0.03 mg/m^3 (15 minutes)	Alkyl mercury 0.01 mg/m^3 (8 hours) 0.04 mg/m^3 (Ceiling)
		Methyl mercury 0.01 mg/m^3 (8 hours) 0.1 mg/m^3 (15 minutes)	Aryl Mercury 0.1 mg/m^3 (8 hours)	Aryl Mercury 0.1 mg/m^3 (8 hours)
		Organic mercury forms 0.01 mg/m^3 (8 hours) 0.03 mg/m^3 (15 minutes)		

1.4.1 Stabilization

The most common remediation treatments employed for soil contamination including stabilization, thermal desorption and washing treatment. Stabilization or solidification is a physical process that could enhance material engineering properties, such as compressive stress, permeability, bearing of erosion and so on. Stabilization could be used in the treatment of elemental mercury or remediation of mercury contaminated soil or sludge. Solid stabilized mass could reduce the chance to release contaminants from it by binding physically contaminates or inducing chemical reaction to reduce the mobility between the media and contaminants [37]. Wang et al. [16] presented that stabilization process use media such as cement, polyester resins, thermoplastics, pozzolan as a binder to form a non-liquid or semi-solid state and immobilize contaminants in sludge. Binder could also be metal such as copper, zinc, nickel to form an amalgam with mercury [37]. Anacleto and Carvalho [38] used metal including zinc, iron and aluminium as reducing agents to remove mercury and found that efficiency depends on the type and surface area of metals. Zhang et al. [39] used

reactive carbon and Portland cement as a binder to treat mercury waste. Zhang et al. [29] chose thiol-functionalized zeolite and Portland cement to immobilize the hazardous mercury. Cement here is used as a binding additive, it often used in stabilization for remediate contaminated sites due to its low price. Bowerman [40] investigated the solidification in treatment of sludge from LANL (Las Alamos National Laboratory) by using cement with sodium metasilicate as binder, the initial mercury concentration is 0.125 mg/L and the final mercury concentration after treated is 0.0014 mg/L averagely. Hulet et al. [41] used Portland cement with liquid sulphide to treat soil which contained an initial mercury concentration about 0.282 mg/L, and the final mercury leachability is 0.0139 mg/L.

The efficiency of stabilization or solidification (S/S) is dependent on the mobility of mercury, which could be impacted by the pH of waste and the properties of mercury compounds. Many studies proved that the lower value of pH is, the higher leachability of mercury. Therefore, keeping an alkaline environment during a mercury decontaminated process could raise a good applicability of S/S. Mercury compounds with a higher solubility, such as mercury sulphate, may form at a higher value of pH. Visvanathan [42] did an experiment trying to study the performance of stabilization in mercury polluted sludge generated from an oil& gas exploration equipment and he used sodium sulphide as a pre-treatment reagent in order to transform mercury into mercuric sulphide, which has a lower solubility at a low pH. Results demonstrated that adding proper amounts of sodium sulphide in sludge could improve the performance of solidification, the ratio of sludge to sodium sulphide is 1:0.2 and the final concentration of mercury is below the Thailand standard (0.2 mg/L).

The advantage of S/S is that it can make mercury more stable and the cost of is not high. However, the volume and mass of contaminated materials have a significant increase during solidification. Moreover, the mercury is not removed from the waste, its leachability is reduced but generates a product that needs further management

such as landfill. A higher mercury concentration in waste, a higher mercury content could be present in leachate.

1.4.2 Thermal treatment

Thermal desorption is a common method of mercury heat treatment. This technology has been used to remove mercury from contaminated solid matrix (especially soil, sludge, sediment and waste) at a full-scale. It heated the contaminated sites without combustion but increase the volatility of mercury which are available removed from the contaminated medium. The boiling point of mercury at one atmosphere pressure is about 350 ºC. All mercury compounds such as HgO, HgS, elemental mercury included in soil or sludge could turn into gaseous elemental mercury when the heating temperature reach 600-800 ºC and the followed condensation system is used to convert these gaseous elemental mercury into liquid phase, which could be collected to reused or be treated further (such as amalgamation with metals for disposal) instead of releasing to atmosphere [16].

Many studies investigated that an effective thermal desorption for mercury remediation depends on the temperature, duration time, soil type, moisture content and organic context. The common temperature range for thermal treatment is from 127 to 700 ºC [43]. Massacci, Piga et al. [44] found mercury concentration with an initial value of 217 mg/kg in soil samples could be reduced to 10 ng/g when heated at 700 ºC for 4 h. Busto, Cabrera et al. [45] reported that remove mercury from waste sludge at temperature higher than 400 ºC is so efficient that the concentration of mercury could be reduced below 0.2 mg/L. Chang et al. [43] concluded that the equilibrium concentration of mercury decreases with a higher temperature. What's more, Chang indicated the thermal treatment for mercury remediation at temperature above 700 ºC during minimum 2 hours performed a great efficiency. Rumayor [46] presented a temperature range of 150 to 600 ºC could give a good performance for

thermal treatment in mercury removal from soil wastes. For mercury contaminated mining fields, the efficiency of remediation could be great at temperature 400 to 650 ºC. However, the temperature needed for thermal desorption of mercury removal in discarded fertilizer equipment is lower (200-350 ºC). Waste material with moisture over 20% to 25% should be treated before loaded into retort unit which is used for thermal desorption. The pretreatment such as mixing with dry materials, will extend the overall processing time and lead to a raise in treatment costs. Besides, high concentration of mercury exist in solid waste can increase the costs of treatment because it demands a longer residence time [37].

Compared to other methods, thermal treatment of mercury could be safer and more efficient. Mercury could be collected and recovered. However, some disadvantages exist as well: due to the requirement of fuel and high energy and of several units (such as distillation and condensation), thermal desorption causes a high cost, so thermal treatment is more suitable for high total mercury concentrations in soil, sludge and waste [42]. What's worse, high temperature required in thermal desorption may change the properties of solid waste and may lead to more contaminants, for example, metal wastes may transform to another compound or lead to repartition at high temperature. Huang et al. [47] worked out a high efficiency of thermal treatment at temperature above 550 ºC by decreasing mercury concentrations from 1320 to 6 mg/kg, but it caused a metal repartition. In order to avoid properties altering, it could pose an operation of thermal desorption at lower temperature with longer time. Kucharski [48] investigated an operating condition designed for the mercury removal in thermal treatment: 100 ºC with time of 10 days, it found that most mercury could be removed and the residual mercury in soil waste is below 30%.

1.4.3 Washing treatment

Washing treatment or chemical leaching is a process which consist of physical

particle separation and chemical treatment used to decrease contaminated contents in contaminated sites [37]. Because most contaminated substance trend to adhere to the finer solid particles rather than the larger particles such as metals and gravel. The physical process could wash larger size particles away from the tiny particles and then concentrate the contaminants bind to the smaller particles for the further chemical treatment. The pre-treated soil, sludge or sediment would mix with a wash solution of applicable chemical reagent to remove hazard mercury. These chemical additives used for removing mercury from sludge or the metal surface of pipeline could be leaching agents such as iodide solution, oxidize agent, acid and so on. The point worth noticing is that this washing technique could only concentrate and remove pollutants (mercury) from contaminated sites but does not eliminate them, so a further treatment to manage the waste solution produced by washing process.

Mercury found in deposits of oil and gas operations are mostly elemental mercury, so washing solutions are selected according to their ability to dissolve liquid elemental mercury in aquatic solution. Many studies showed that solution involving iodine as an oxidizing agent and iodide (potassium iodide) as a complexing agent is efficient to dissolve metallic mercury, as shown in equation (1), the existence of iodide could increase the solubility of mercury and iodine due to the formation of tri-iodide. This solution is highly efficient in mercury decontamination, the efficiency is more than 90% [49].

$$I_2 + 2I^- \leftrightarrow I_3^- \quad (1)\ [16]$$

Many extracting agents have used to test the ability of dissolving metal, such as hydrogen peroxide (H_2O_2), cyanide, potassium persulfate ($K_2S_2O_8$), iodine, nitric acid (HNO_3), thiosulfate and EDTA. EDTA is suggested as the applicable reagent to treat the heavy metal contaminated sites, it can produce a high efficiency above 30% for the mercury remediation of soil [16]. Zhou et al. [50] used 500 ml hypochlorite leaching solution to dissolve 0.5 g elemental mercury in lab scale and got a mercury

extracted percentage of 63% after about 21 h contacting. Potassium iodide and iodine solution can also dissolve gold with high efficiency due to the similar properties of gold to mercury. Isaia et al. [51] compared the efficiency on oxidation of gold between many lixiviants. It was found that a 99% gold recovery efficiency was achieved by using iodine (2 g/L) and iodide (12 g/L) solution, whereas the efficiency of gold recovery was 80%, 93%, 84% and 65% by using ammonium thiosulfate, cyanide, thiourea and mbtt/iodine respectively.

Iodine should be used with potassium iodide or other halogen salts in case of an impact on the properties of solid medium [16]. What's more, the concentration and the ratio of iodide to iodine and other factors such as solution pH, reaction time and temperature would influence the dissolution of mercury. It's reported that some brown fine precipitate was formed when the solution of iodine and iodide contact with a given mass of mercury, this sediment could be dissolved by adding additional potassium iodine, so it's necessary to analyze the ratio of I^-: I_2 and usually an excess of iodide is preferred. Chaiyasit [49] accessed a mercury level both on the surface and in the depth of metal oil pipeline and then studied the optimal concentration of iodide/iodine solution used in decontamination of mercury. During the experiment, the concentration of iodine ranged from 0 to 1.0 M and every solution had the same amount of potassium iodide (2 M), it found that these solutions with various concentration of iodine did no significant differences in the performance of dissolving elemental mercury and concluded the 0.2 M solution is the most optimal concentration, which could remove more than 99% mercury. Barbara [52] designed a test to study whether the concentrations or molarities of iodine-iodide could influence the extraction of mercury from the solid waste. Using concentrations of leaching solution (pH = 4): 0.025 M KI to 0.0125 M I_2, 0.05 M KI to 0.025 M I_2, 0.1 M KI to 0.05 M I_2 and 0.2 M KI to 0.1 M I_2. It was found that the solution at, or above, 0.2 M iodide and 0.1 M iodine could remove more than 99% of mercury with an initial concentration of 774 mg/kg. Barbara also tested the influence of solution pH and found that the optimal pH for the

mercury remediation is 4, with a residual mercury concentration of 2.7 mg/kg, other solutions at pH of 5 and 7 had resulted in a final concentration of mercury with 39 and 42 mg/kg respectively. The reason why pH could affect the performance of washing process is that a specific value of pH could influence the solubility of contaminants which are extracted from a waste matrix at particular pH range [37]. The halogen of iodine could also be replaced by bromine or chlorine. Cai et al. [53] made a comparison between potassium iodide (KI) and potassium bromide (KBr) to see their ability to extract mercury from clay, it found that KI performed a higher capacity of dissolving mercury than KBr.

The benefits of chemical leaching are that it can remove mercury with high efficiency and it certainly not increase the volume or mass of contaminated materials, washing treatment could flush away contaminants with water or chemical leaching solution to allow contaminated materials (such as oil pipelines) to reuse or recycle, which could decrease potentially cost used for cleaning or disposal of wasted materials [37]. For small amount of mercury contaminated matrix, washing treatment can be selected for the lower cost. Additionally, chemicals used in leaching are seldom emitted to air during the washing process, so this method is relatively safer to the environment and worker. However, the large requirement for water used for preparing washing liquid or leaching solution is one disadvantage of chemical leaching. Also, washing method cannot destroy mercury and need a further treatment such as precipitation and ion exchange. One limitation of washing method is that it’s not useful when the soil contains high percent (more than 40%) of silt or clay.

1.4.4 Precipitation

Chemical precipitation could be used for capturing mercury from the contaminated wastewater or the leachate generated by washing treatment. It forms insoluble precipitate or coagulant by using specific chemicals to mix with dissolved metals and

then followed by a separation process (filtration, gravity setting) to separate the mercury-containing solid from wastewater. Sulphur precipitation is the most common method used in inorganic mercury removal from aquatic waste. Blue et al. [54] used $BDTH_2$ (N,N′-bis(2-mercaptoethyl)isophthalamide) to capture mercury washed from gold mining and found high efficiency for precipitation at neutral pH, reduced mercury contents from 40 mg/kg to 8 μg/kg. It was reported that a more than 99% removal efficiency can be achieved by sulphide precipitation when initial mercury concentration is more than 10 mg/L. The lowest achievable wastewater mercury level present to be about 10 to 100 ppb, it's hard for sulphur precipitation to reduce mercury levels under approximately 10~100 ppb, therefore, sometimes it's need a secondary process such as ion exchange or adsorption to achieve a lower mercury concentration. [37, 55]. Table 1-4 shows some reported examples of mercury extraction from aqueous solutions by precipitation. The limitation of mercury discharge ruled by the United States Environmental Protection Agency (EPA) is 0.2 ppm [56].

2,4,6-Trimercapto-s-triazine, trisodium salt (TMT-15) is widely used in disposing wastewater containing heavy metal in industries because of its high efficiency in capturing mercury by forming a stable insoluble precipitate over a wide pH (6-10) and it doesn't produce dangerous substances [57]. Adjusting pH of waste water is important to the removal of mercury because the efficiency of removal could get a maximized value at a pH where the precipitate is maximum insoluble. Henke [58] reported that TMT-15 could form stable white gel with mercury chloride solutions at pH 6 to 7, with a higher dosage of TMT the precipitation could turn into yellow or green and pH should increase to 11 or 12. What's more, the Hg-TMT complexes are thermally stable, Lu et al. [59] used TMT-15 to treat gas field wastewater with high concentration of mercury, and found the quality of Hg-TMT complexes only had a slight loss when they were calcined at 250 ºC for 120 min, the chemical bond of the chelate product is so strong that make it difficult to break down at high temperatures.

Table 1-4 Reported mercury extraction by precipitation.

Precipitate Agent	Time/h	pH	Initial Hg concentration	Final Hg concentration	References
sodium dimethyldithiocarbamate (STDC)	1	4	50 ppm	1.01 ppm	[56]
2,4,6-Trimercaptotiazine, trisodium salt (TMT).	1	5.5	50 ppm	18.07 ppm	[56]
potassium/sodium thiocarbonate (STC)	1	6	50 pm	8.59 ppm	[56]
Thiosulfate	4	4	2 g/l	10 ppb	[50]
TMT-55	6	7	0.07-0.13 M	0.28 mg/l	[58]
Sodium hydrosulfide	5	3	13.15 ppm	10-50 ppb	[60]
1,3-benzendiamidoethanethiol ($BDET^{2-}$)	0.25	0-14	34.5 ppm	0.008 ppm	[61]
Sodium hydrosulphite	4	7	149 ppm	0.745 ppm	[5]

Another commonly used method of chemical precipitation to extract inorganic and organic mercury from wastewater is coagulation. The major coagulants applied to coagulation are ferric salts (ferric chloride, ferric sulphate or ferric hydroxide), aluminium and limestone [62]. The dominant mechanism of mercury removal is adsorption and co-precipitation. The mercury-containing solids are formed by adsorption of ions into bulk solid , for example, precipitate of aluminium hydroxide and iron hydroxide is formed by adding alum and ferric salt respectively [62]. Lu et al. [63] used Mn-Fe (hydr)oxides to remove mercury(II) from aqueous solution, with a consequence of 80% removal efficiency, mercury concentration was reduced from 30 ppm to 5 ppm, it was concluded that Mn-Fe hydroxide had a higher removal efficiency than iron (III) chloride ($FeCl_3$) and poly-aluminium chloride. pH has an important impact on the removal of mercury from solution by co-precipitation, Lu concluded that the higher mercury removal efficiency can be obtained at higher pH of solution, Hg removal increased from 3% to 87% when pH raised from 5 to 8 [63].

Precipitation is highly efficient and quick to extract mercury from aqueous solutions or waste water via some specific sulphide chemicals, but it generates mercury-containing residual sludge, these sludges should be treated as hazardous solid waste and need a further treatment such as solidification to dispose them to avoid additional contamination to the environment. The efficiency of mercury precipitation is highly dependent on pH adjustment of effluent. Generally, mercury removal efficiency has a maximum value at the pH where the precipitate is least soluble: for sulphide precipitation process, the highest removal efficiency could be obtained within a pH range of 7 to 9; for hydroxide precipitation/co-precipitation, the most effective precipitation of mercury achieved at pH 7-11 [37]. Another disadvantage of chemical precipitation is the influence of other metals in water, the removal efficiency of mercury may be impacted by the present of other metals. In addition, a single step of precipitation may not realize the decontamination goals, additional treatments or multiple precipitation steps may be required to achieve strict cleaning goals or disposal standards.

1.4.5 Ion exchange

Ion exchange is a kind of interchange of ions between a solid material (such as ion exchange resin) and a liquid. It provides a method to remove soluble mercury from waste streams. Mercury in the form of anionic complexes such as $[HgCl_3]^-$ can be managed by anion exchange resins. On the contrary, cation resins such as which contains thiol group could exchange cationic mercury selectively. Monteagudo [64] selected a commercially available polystyrene-divinylbenzene resins to capture mercury in mine wastewater from an initial concentration of 90 ppm to a final concentration of 34 ppb. One advantage of resins is that it has selectivity of mercury over other metals such as ions of copper, iron, nickel and platinum. Resins such as Duolite ES-466, Diaion CR-I0 and Amberlite IRC-718 have a great selectivity of mercury exchange. Yavuz et al. [65] grafted polyacrylamide on spherical polyvinyl

pyridine resin and found it had a high capacity for exchange mercury and the resin was highly selective of mercury. Ion exchange resin is highly efficient on mercury removal but it also may lead to a change of effluent quality caused by ion exchange. Duolite GT-73 is a kind of acid cation thiol resin and it can decrease mercury from a concentration of 200-70000 ppb to 1-5 ppb [37]. Chiarle [66] removed mercury from wastewater by adsorption of using Duolite GT-73 resin and reported that this played a great performance on the adsorption of mercury with high capacity and removal efficiency of approximately 100%. Lloyd et al. [67] used Duolite GT-73 and chelating ion exchange resin Purolite S920 to compare their ability on mercury sorption from aqueous solution, it was found that S920 can remove mercury faster and achieve a 78% mercury removal efficiency at 2 min, however GT-73 only achieved 25% removal.

The benefit of ion exchange include: high efficiency on mercury removal, can achieve a very low level (mercury-free) of effluent contaminant; High selectivity of mercury; insensitive to variability. The disadvantage is: result in a regenerate brine that must be disposed of. Table 1-5 collates data for a series of different ion exchange resin showing their reported effectiveness for removing mercury from water.

Table 1-5 Ability of mercury removal of different ion exchange resin

Ion exchange resin	Resin Type	Initial Hg concentration/ ppb	Final Hg concentration/ ppb	References
Duolite GT-73	weak acid cation thiol	200-700	1-5	[37]
Purolite s920	Chelating thiouronium	10.67	0.34	[60]
Purolite s924	Chelating thiol resin	10-2500	< 5	[68]
AFP-329	Weak base anion resin	12.21	0.44	[60]
Dowex 1X8	Strong base anion resin	24500	5	[5]
Dowex XZS-1	Strong base cationic resin	7000-9000	34	[64]
ASB-2	Strong base anion resin	14.31	0.70	[60]
Lewatit MP64	Weak base anion resin	250000	21000	[69]
Lewatit TP-214	Cationic resin with S and N groups	250000	7000	[69]

Chelating resin is one type of ion exchange resin, it's generally consisted of two parts of chelating groups and poly matrix [70]. Compared with the ion exchange resin, chelating resin can bond with metals strongly and has higher selectivity, it can be widely used in a variety of metal ions recovery and separation. Purolite S924 and S920 are polystyrene based a kind of chelating resin designed for the selective removal of mercury (and platinum group metals) for water treatment. They have high reported capacities for mercury of up to 200 g/L and can reduce mercury concentration from 2-20 ppm to less than 5 ppb [68, 71], their properties of mercury capture are not impacted by high concentrations of chloride or sulphate in the effluent streams. Ferreira and Carvalho [69] applied anion resin Lewatit MP64 to remove mercury from chloro-alkali plant waste water, the removal efficiency was reduced with the increasing concentration of chloride in solutions due to the competition between $[HgCl_4]^{2-}$ and Cl^-. The functional group of Purolite S924 is a thiol. Thiol resins form stable thiol-mercury(II) complex due to the favored interaction between the S sites and Hg [72]. If two thiol groups are favorably spaced or at low mercury concentration, as illustrated in figure 1-4: two groups can form a linear two-coordinate complex with one mercury (II) ion. Purolite S920 is thiouronium type resin, complexes are formed by the coordination bonds between Hg^{2+} and S and, N sites in the complexant. Table 1-6 shows the main characters of Purolite S924 and S920.

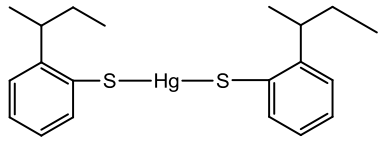


Figure 1-4 Structure of 2:1 thiol-mercury complex [72].

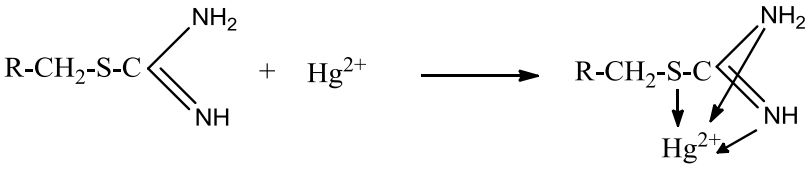


Figure 1-5 Reaction of thiouronium resin capturing soluble mercury(II) [72].

Table 1- 6 Properties of Purolite S924 and Purolite S920 resin [71, 73]

Characteristics	Purolite S924	Purolite S920
Type	Chelating resin	Chelating resin
Functional group	Thiol	Thiouronium
Ionic form	H^+	H^+
Capacity	200 g/L Hg	200 g/L Hg
Physical form	Spherical beads	Spherical beads
Mean size typical	0.55-0.8 mm	0.60-0.85 mm
Moisture retention	45-51%	48-54%
Polymer structure	Macroporous crosslinked polymer	Macroporous crosslinked polymer
Specific Gravity	1.10 g/ml	1.11 g/ml
Temp limit	60 ºC	80 ºC
pH limit (operating)	1-11	1-10
Remark & Applications	High selectivity for mercury removal in wastewater.	High selectivity and high capacity of mercury removal in effluent. Widely applied as final polishing to meet mercury discharge limits. Selective recovery of precious metals (Au, Pt, Pd, etc) from acidic solutions.

Except all the methods mentioned above, there have many other remediation treatments to remove mercury, such as verification for soil waste, membrane separation, adsorption, biological treatment for wastewater. What's more, some emerging and ongoing methods appeared and need to further study: nanotechnology, phytostabilization, air stripping and electro-remediation.

1.5 Remediation treatment applied to experiment

Consider the practical condition of oil and gas pipeline decontamination and

decommissioning, mercury deposit in plant is a kind of solid contamination, washing treatment using KI/I_2 solution is recommended on this occasion, because leaching is more efficient, suitable and has a lower cost to extract metallic mercury compared to other treatment such as solidification and thermal treatment. KI/I_2 solution is reportedly efficient to dissolve elemental mercury, a modified system of halide salts solution such as Br^-/I_2, Cl^-/I_2 or Br^-/Br_2 is seldom investigated and used to treat elemental mercury. KBr, NaBr, KCl and NaCl solutions, as substitutes for KI were also studied in order to determine whether these salts combined with iodine as oxidant were efficient for mercury dissolution.

After mercury dissolution in tri-halide solution, a further treatment is needed to extract soluble mercury from solutions and ensure the waste water is Hg-free. The two approaches under investigation use (i) a commercial precipitant, TMT-15 and (ii) Purolite S924/S920 ion exchange resins are applied comparatively to concentrate and capture Hg (II) from solution. In either case, mercury decontamination from pipeline can be realized and achieved.

Chapter 2

Dissolution of elemental mercury in KI/I_2 solution

2.1 Experimental

2.1.1 Materials and instruments

Liquid elemental mercury was purchased from Sigma-Aldrich (98%) and prepared for dissolution.

A series of standard potassium iodide/iodine solutions with 3:1 iodide:iodine molar ratio were prepared by dissolving solid potassium iodide (Fisher Scientific) and iodine (Fisher Scientific) in deionized water within a 100 ml volumetric flask. Solutions were prepared at 2% (0.027/0.081 M I_2/KI), 3% (0.04/0.12 M I_2/KI), 4% (0.053/0.16 M I_2/KI), 5% (0.067/0.2 M I_2/KI), 6% (0.08/0.24 M I_2/KI) w/v (g/ml).

pH values of solutions were adjusted by addition of small volumes of 0.1 M solutions of hydrochloric acid, sodium or potassium hydroxide, testing the pH value using a Thermo pH meter.

All samples were stirred at an electric magnetic stirrer plate (Variomag).

2.1.2 Analysis of mercury content in KI/I_2 solutions

Mercury concentrations in samples were measured using a Milestone DMA-80 total mercury analyser. The DMA-80 is a direct mercury analyser and is used for element specific determination of mercury in solids and liquid samples by thermal decomposition, and then amalgamation followed by mercury desorption and detecting by atomic absorption spectrophotometry [74]. Sample analysis is rapid, taking approximately 7 minutes and does not require chemical pre-treatment. The key limitation of the DMA-80 analyser is that the maximum mercury content that can be determined is approximately 1000 ng, and if larger mercury samples are run, they can result in condensation inside the analyser and contamination. Because the initial

elemental mercury mass used for dissolution screening experiments here was 100 mg, the maximum mercury concentration of solution after complete dissolution could be about 10000 ppm. In order to ensure that solutions for analysis (100 μL) would not contain more than 1000 ng of mercury, a sequential dilution sequence was used. All samples use for testing dissolution were diluted by a factor of 100000 before test, the methodology is described below:

(1) A 10 μL sample from of the soluble mercury solution was taken using a pipette (GILSON, 2-20 μL), then diluted to 10 cm^3 in a volumetric flask with deionized water, to prepare a solution with $[Hg]_{max}$ <10 ppm. (2) For analysis, a 100 μL sample from the diluted $[Hg]_{max}$ < 10 ppm solution was transferred by pipette (RAININ, 20-200 μL) into DMA-80 quartz sample boats for analysis.

Here is a brief procedure of how to test mercury content in KI/I_2 solution:

(1) Dilute the dissolved mercury solution by using deionized water;

(2) Weight liquid samples (100 μL, about 0.1 g) into a sample quartz boat and transfer the sample weight from the analytical balance to the DMA-80.

(3) Sample boats are loaded onto the instrument auto-sample.

(4) After 7 minutes analyzing by DMA-80, read the mercury content on screen.

Three replicate tests were achieved for the assessment of errors.

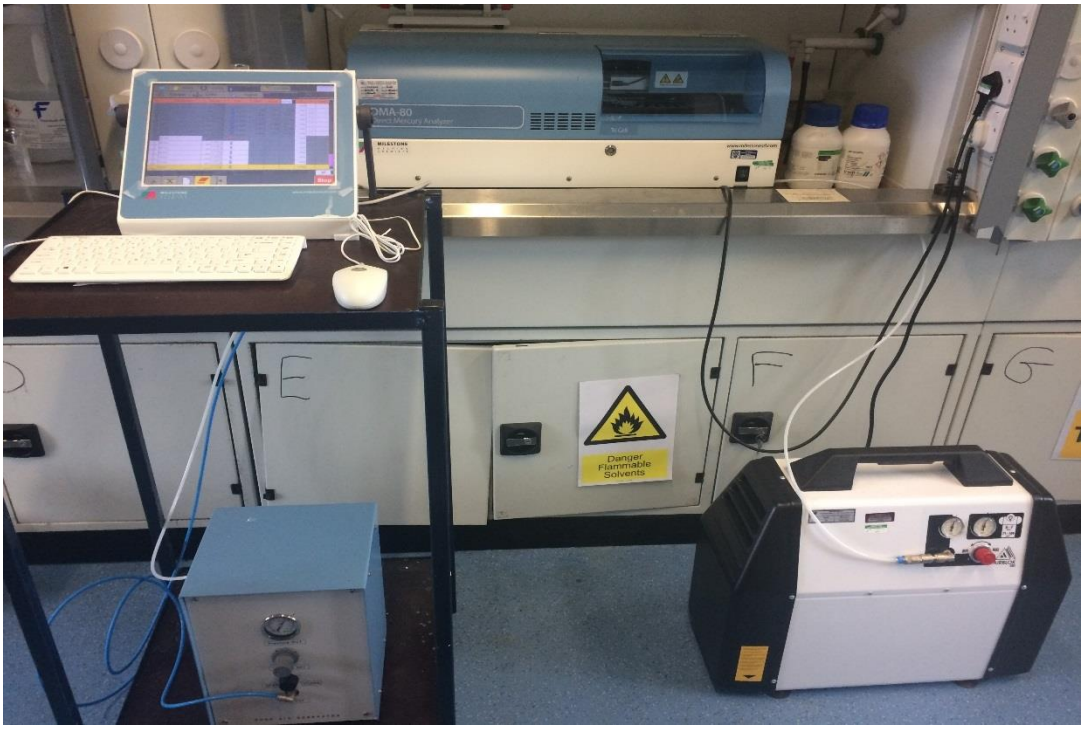


Figure 2-1 Milestone DMA-80

2.1.3 Solvent optimization of potassium iodide and iodine solution.

The impact of KI/I_2 solution concentration on the dissolution efficiency of mercury was studied. A small quality of elemental mercury (~100 mg) was contacted in the following solutions of KI/I_2 (the weight details are shown in Table 2-1): 6%, 5%, 4%, 3% and 2% weight/volume (w/v, g/ml), respectively. The “expected mercury solubility” in Table 2-1 is the expected maximum mercury that can be dissolved in solutions, it’s calculated based on the mole of iodine (1:1 Hg: I_2). The volume of each KI/I_2 solution was 10 ml. Dissolution of mercury were taken place in closed glass vials, at room temperature (25 ºC) with a magnetic stirring at 50 rpm for 24 h. The mercury content the solutions after 24 h contact was determined by analysis using the DMA-80, after sample dilution as described in section 2.1.2.

Table 2-1 Data of the amount of potassium iodide and iodine in different concentration.

Concentration w/v	solute	g in 100 ml	Moles/liter	Moles in 10 ml	Expected mercury solubility mg (1:1 with I_2)
2%	I_2	0.68	0.027	0.00027	54
	KI	1.32	0.081	0.00081	
3%	I_2	1.01	0.040	0.00040	80
	KI	1.99	0.120	0.00120	
4%	I_2	1.34	0.053	0.00053	106
	KI	2.66	0.160	0.00160	
5%	I_2	1.70	0.067	0.00067	134
	KI	3.30	0.200	0.00200	
6%	I_2	2.02	0.080	0.00080	160
	KI	3.98	0.240	0.00240	

2.1.4 Influence of I_2/KI ratio

The influence of I_2/KI ratio on the dissolution of mercury was studied in a similar way as described in section 2.1.3. In each case, element mercury (100 mg) was contacted with I_2/KI solutions (10 cm^3) with differing I_2:KI molar ratios between 1:1 to 1:4, 1:1 (0.053/0.053 M), 1:2 (0.053/0.106 M), 1:3 (0.053/0.16 M) and 1:4 (0.053/0.212 M), contacting at 25 ºC for 24 hours with stirring before dilution and analysis.

Table 2-2 Data of the amount of potassium iodide and iodine in KI/I2 ratio.

I_2:KI	solute	g in 100 ml	Moles/liter	Moles in 10 ml	Expected mercury solubility mg (1:1 with I_2)
1:1	I_2	1.34	0.053	0.00053	106
	KI	0.88	0.053	0.00053	
1:2	I_2	1.34	0.053	0.00053	106
	KI	1.76	0.106	0.00106	
1:3	I_2	1.34	0.053	0.00053	106
	KI	2.66	0.160	0.00160	
1:4	I_2	1.34	0.053	0.00053	106
	KI	3.52	0.212	0.00212	

2.1.5 Influence of pH

To examine the effect of pH on extraction, the pH of standard solutions of aqueous KI/I_2 (10 ml each) with overall concentration of 4% w/v (0.053/0.16 M I_2/KI) were varied by addition of drops of either 0.1 M hydrochloric and 0.1 M potassium hydroxide to adjust the solution pH to 1, 2, 3, 5, 6, 7, 9, 11 respectively. Mercury dissolution tests were then conducted as previously described. Over 24 hours at room temperature.

2.1.6 Influence of contact time and temperature

The influence of temperature on the dissolution process was tested over the temperature range 25-65 °C at five temperature points (~25 °C, 35 °C, 45 °C, 55 °C, and 65 °C). Higher temperatures were not investigated due to the potential losses of volatile iodine from solutions due to sublimation. Samples (10 µL) were taken from each solution as fixed times between 15 min-24 h to assess the rate of dissolution.

Five vials with 10 ml potassium iodide and iodine (3:1) solution of 4% w/v should be prepared and put on the hot plate to adjust to the temperature above. The amount of elemental mercury was 100 mg for each vial. Putting magnetic stir into each vial to stir the solution and took samples from it at different time points to analyse the mercury concentration. The time point should be taken as a timeline from 15 min to 24 h until the dissolution of elemental mercury in potassium iodide and iodine solution reached a maximum solubility. The volume sampled for each time was limited to 10 µL in order to ensure that no significant overall volume changes were made to the vial. The sample was then diluted it in a 10 ml volumetric flask by using deionized water.

2.2 Result and discussion

Approximately 100 mg of elemental mercury was added to each 10 ml leaching solution for dissolution experiments. Therefore, the maximum concentration of mercury that can be achieved in solution after a complete dissolution is 0.05 M for 100% efficiency for mercury oxidation and solubilisation. This is a high content of mercury, and experimental errors of results are mainly come from the dilution of solution and calibration of DMA-80. Consider the error and collect a mass of data, when the concentration of mercury tested by DMA-80 was within a range of 0.049 to 0.053 mol/L, or the solubility efficiency was from 99% to 106%, it could be considered as a full dissolution of mercury because there was no unreated mercury or precipitate left in leaching solutions. The error is standard deviation of a triplicate test.

2.2.1 Influence of leachate concentration

The effect of the concentration of potassium iodide/iodine extractant in solution of mercury dissolution was determined using 5 concentrations with the solute/solvent ratio of 2% (0.027/0.081 M I_2/KI), 3% (0.04/0.12 M I_2/KI), 4% (0.053/0.16 M I_2/KI), 5% (0.067/0.2 M I_2/KI), 6% (0.08/0.24 M I_2/KI) w/v (g/ml). From Table 2-1, based on the oxidation of Hg (0) to Hg (II) by one mole of I_2, it was anticipated that the 2% and 3% KI/I_2 solutions would not completely dissolve all of the mercury present in the test samples, whereas those solutions containing at least 4 wt% oxidant should be capable of complete dissolution of the 100 mg Hg present. The results (Fig.2-2) confirm that the dissolution of mercury increased with an increasing concentration of KI/I_2 solution.

After the 24 h contact, the initial dark brown potassium iodide/iodine solutions changed colour to pale yellow clear solution, as iodine is converted to iodide during the oxidation of Hg (0) to Hg (II). In the solutions with 2% and 3% w/v of extractant,

residual mercury was observed in the bottom of the vials, and after analysis 44.5±3.0% and 78.3±1.6% of the elemental mercury added was found to be in solution. These results correspond well with the theoretical solubility limits of ~54 and ~80% respectively calculated on the basis of the I_2: Hg (1:1) concentration ratios. With the 4% solution, all the 100 mg mercury was completely dissolved. No residual elemental mercury or insoluble mercury complexes precipitate were observed in the test mixtures. Mercury concentrations of 0.050±0.002 mol/L was achieved using the 4% w/v KI/I_2 solutions, the dissolution efficiency was 100.7±3.8%. Considered the measurement errors, these results were accordant well with the theoretical solubility efficiency of 100% calculated on the quantitive basis of 1:1 ratio of $Hg:I_2$. Because the initial mercury amount added into solution was 100 mg, the concentration of iodide/iodine of 5% and 6% w/v solution is in excess of that required to dissolve all 100 mg mercury assuming a 1:1 Hg (0):I_2 ratio is needed for oxidation of Hg (0) to Hg (II). After complete dissolution, the mercury concentration in solution will be 0.05 M. The concentration of mercury found after analysis in 5% and 6% solution was 0.050±0.003 and 0.049±0.002 mol/L, where corresponding a solubility efficiency of 100.6±5.2% and 99.9±4.1% respectively. Iodine is relatively volatile at elevated temperatures, and can be easily sublimed especially from concentrated solutions [5], to avoid iodine evaporation and to achieve less chemicals consumption, the optimal and minimum concentration of KI/I_2 solution to achieve a complete dissolution of mercury is 4% w/v.

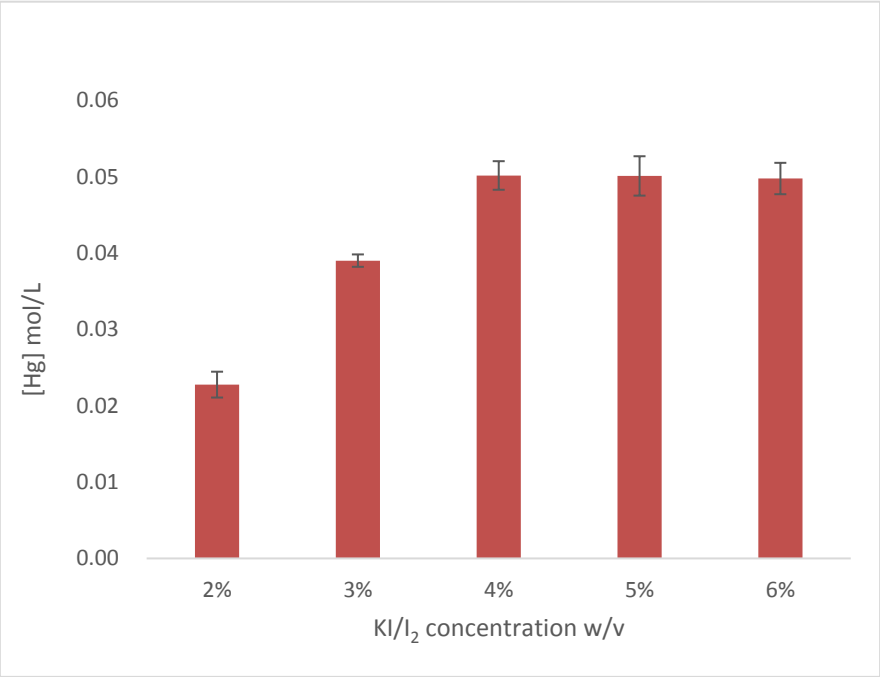


Figure 2-2 Influence of potassium iodide/iodine (3:1) concentration on the dissolution of elemental mercury. 100 mg mercury, 10 ml, 24 h, room temperature, pH 5, 50 rpm stirring. The mercury concentration of 0.05 mol/L corresponds to 100% of available mercury dissolved in these tests. The error is standard deviation from triplicate measurement.

An increase of KI/I_2 concentration could not only increase the concentration of dissolved mercury, but also can increase the rate of dissolution. As shown in Fig.2-3, KI/I_2 solution at concentration of 6% could reach an equilibrium of dissolution at 4-5 h, where achieved a mercury concentration of 0.051±0.001 mol/L. Whereas, it took about 10 h for 4% w/v KI/I_2 solution to reach the equilibrium.

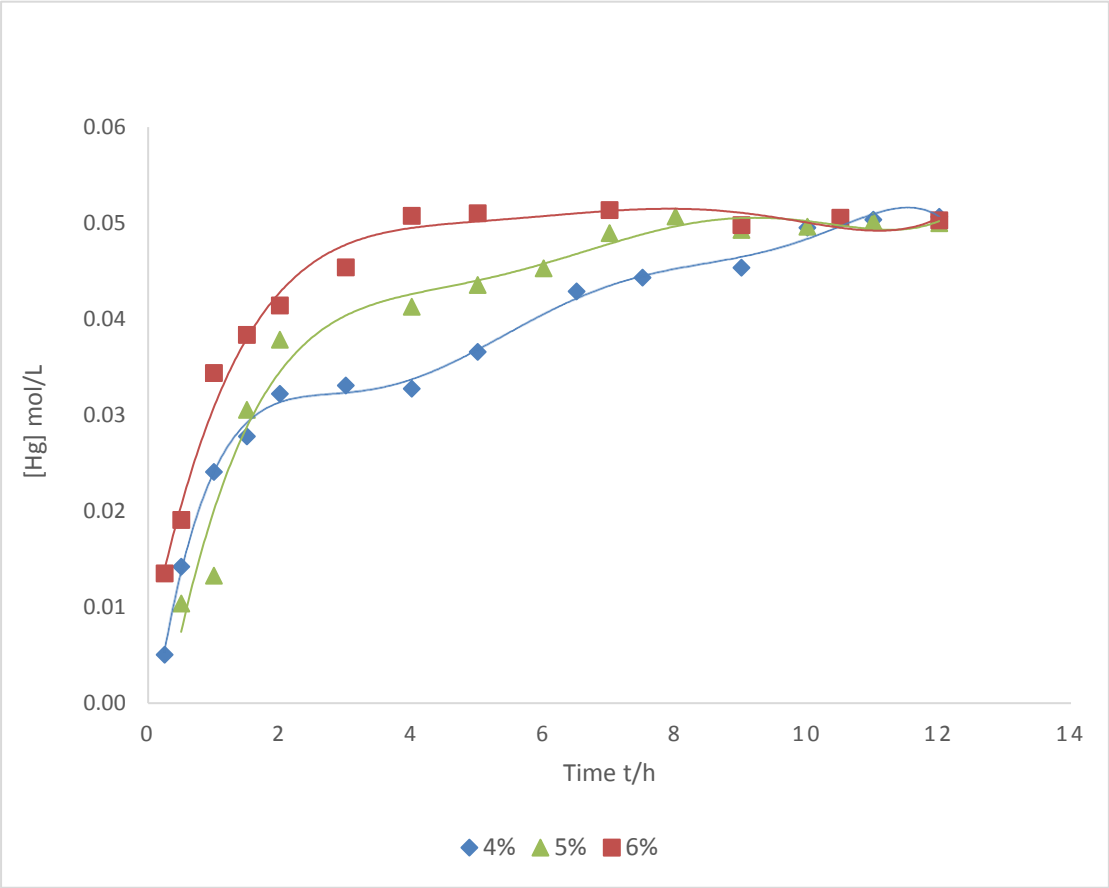


Figure 2-3 Concentration of dissolved Hg versus time profile at three different concentration of KI/I_2 solution. 100mg mercury,10 ml of KI/I_2 solution,24 h, room temperature, pH 5, 50 rpm stirring. The mercury concentration of 0.05 mol/L corresponds to 100% of available mercury dissolved in these tests.

$$\text{Hg Solubility\%}=\frac{\text{Dissolved Hg in solutions}*10^{-6}*100000}{\text{The amount of initial Hg}}*100 \quad (2)$$

$$\text{Hg concentration}=\frac{\text{Dissolved Hg in solution}*10^{-9}*100000}{200.59\ \text{g/mol}*10\ \text{ml}*0.001}\ \text{mol/L} \quad (3)$$

Where the dissolved amount of Hg in solutions is tested by DMA-80, the unit is ng; Samples are diluted by a factor of 100000 for analysis; The amount of initial Hg is 100 mg.

2.2.2 Influence of ratio I_2:KI

Both iodine and iodide are needed to oxidatively dissolve elemental mercury. Iodine is used as the oxidant, and as shown in section 2.2.1, complete dissolution of the mercury added to the test systems was observed when a 1:1 molar ratio of iodine: mercury was used, corresponding to oxidation of elemental Hg(0) to Hg(II). However, the reaction of mercury with iodine will only produce mercury iodide (HgI_2) which is an essentially insoluble material (solubility in water is 0.006 g/100 mL). The role of the added iodide, as shown in equation (4) is to further shift the equilibrium of HgI_2 towards the more soluble tetraiodomercurate(II) ($[HgI_4]^{2-}$) anion. From equation (4), the stoichiometric ratio of potassium iodide and iodine needed for the formation of $[HgI_4]^{2-}$ is 2:1.

$$\mathrm{Hg(l) + I_2 + 2I^- \leftrightarrow HgI_4^{2-}} \qquad (4)\ [16]$$

Figure 2-4 illustrates the effect of molar ratio on the dissolution of mercury. When the treatment solution contains KI: I_2 at a ratio of 1:1 (0.053/0.053 M)，the solubility of Hg is limited, and only 61.5±6.6% of the elemental mercury added was dissolved in the K//I_2 solution, forming a solution with Hg concentration of 0.031±0.003 M. The remaining mercury was converted into the insoluble beta form mercury (II) iodide, which can be visually observed as pale yellow precipitate in the solutions. This precipitate could be dissolved by adding additional potassium iodide, confirming that the equilibrium position in the reaction (equation (4)) could be shifted. At I_2:KI (0.053/0.106 M) ratio of 1:2, after contacting for 24 hours, the dark brown KI/I_2 solution became pale clear yellow solution and all the elemental mercury (0.5 mmol) was formed as soluble $[HgI_4]^{2-}$ with a solution concentration of mercury of 0.051±0.024 mol/L. This corresponds to dissolution efficiency of 101.5±5.8%. When the ratio of I_2: KI was 1:3 (0.053/0.16 M) and 1:4 (0.053/0.212 M), a same phenomenon was observed as with the 1:2 ratio system and no elemental mercury or precipitate was

observed in the KI/I_2 solution vials, the concentration of mercury in solutions was 0.051±0.024 and 0.050±0.027 mol/L respectively. On the basis of eq. 4, a 2:1 ratio of KI: I_2 was confirmed to be necessary to achieve full dissolution of mercury. According to Le Chatelier's principle, increasing the concentration of iodide ions create a "stress" to shift the system to equilibrium. What's more, the presence of I^- could reduce the evaporation of I_2 due the formation of stable I_3^-, and the rate of iodine evaporation reduces with an increase of molar ratio of iodide to iodine [75]. Therefore, there can be advantages in using an excess of potassium iodide, in this case, the ratio of potassium iodide to iodine for the following experiment was fixed at 3:1 in order to ensure that all mercury oxidised was transformed into the soluble anionic form.

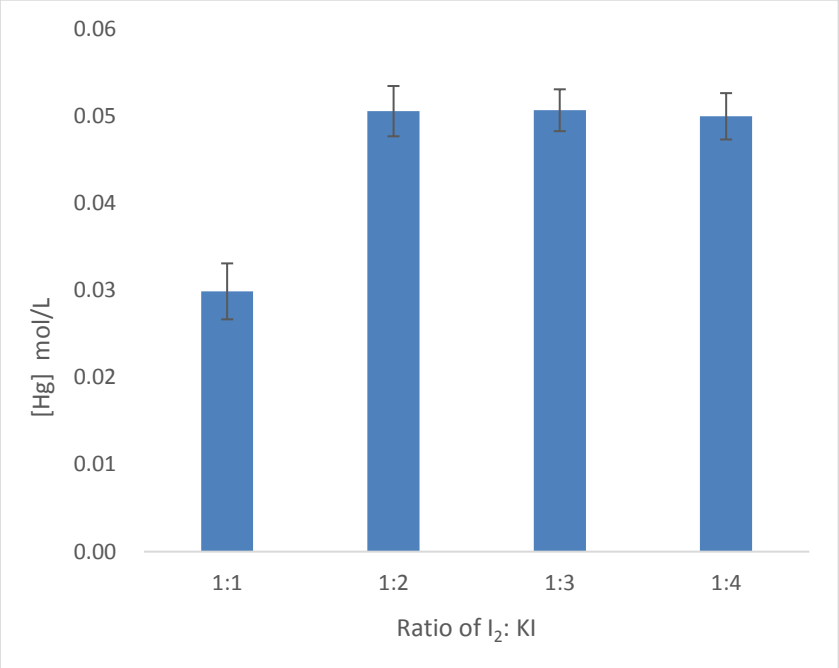


Figure 2-4 Influence of molar potassium iodide/iodine ratio on the dissolution of elemental mercury, 100 mg mercury, 10 ml, pH 5, 0.05 3M iodine solution, 24 h, room temperature, 50 rpm stirring.

2.2.3 Influence of pH

The influence of solution pH on the dissolution was investigated and the results are

shown in Fig.2-5. Dissolution of mercury was limited when the solution was alkaline (pH > 7) and unreacted elemental mercury was observed in the samples after treatment. The concentration of dissolved Hg at pH 9 and pH 11 was 0.033±0.003 mol/L and 0.001±0.001 mol/L, corresponding to approximately 65% and 2% extraction respectively. The tested initial pH value of potassium iodide and iodine solution in this experiment was 5.76, the concentration of Hg after leaching for 24 h was 0.051±0.004 mol/L. Over the pH range 1-7, no significant impact on the dissolution of mercury was observed. In all cases, complete solubilisation of the elemental mercury added was observed, producing solutions containing approximately 0.05 mol/L of mercury. It's suggested to adjust the solution under a mild or neutral condition in order to avoid/minimize dissolution and corrosion of other metals of the plant during the decommissioning process, because metal is easily corrosive and dissolve under acid conditions.

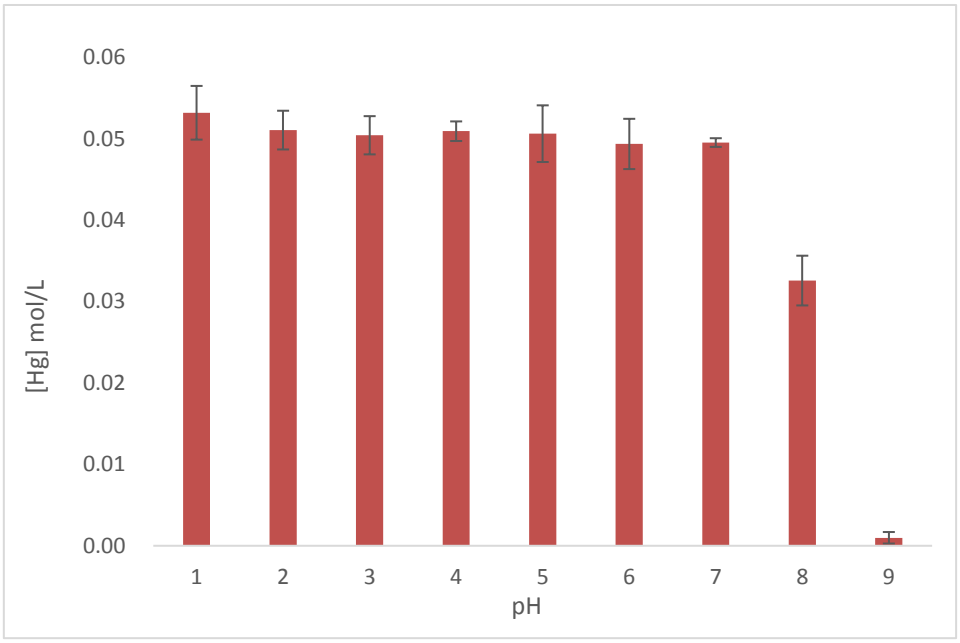


Figure 2-5 Influence of pH on potassium iodide and iodine solution. 100 mg mercury, 10 ml, 4% w/v concentration of KI/I_2 (0.16/0.053 M) solution, 24 h, room temperature, 50 rpm stirring.

2.2.4 Influence of temperature

The effect of temperature on dissolution was investigated over a range from room temperature (25 ºC) to 65 ºC. Figure 2-6 indicates a higher temperature can increase the rate of dissolution, hence reduce the contact time. At room temperature, it took about 10 hours for 10 ml KI/I_2 (0.16/0.053 M) solution to dissolve all 100 mg (0.05 M) and its dissolved mercury concentration at 10 h was 0.050±0.002 mol/L. It took about 7, 6, 5 h to dissolve all elemental mercury at 35, 45, 55 ºC respectively, there was no mercury and precipitate left in the KI/I_2 solutions which contained dissolved mercury at concentrations of 0.050±0.001, 0.051±0.003, 0.050±0.002 mol/L respectively. At 65 ºC, the rate of dissolving mercury was initially faster than the results at lower temperatures, however, the dissolved mercury concentration did not increase after 4 h with the end point containing some unreacted elemental mercury. After 24 h contact time, the concentration in solution was 0.046 mol/L. It was surmised that incomplete dissolution was due to physical losses of iodine from solution due to its volatility at 65 ºC [5, 76]. The evaporation rate increases with an increasing of temperature [75].

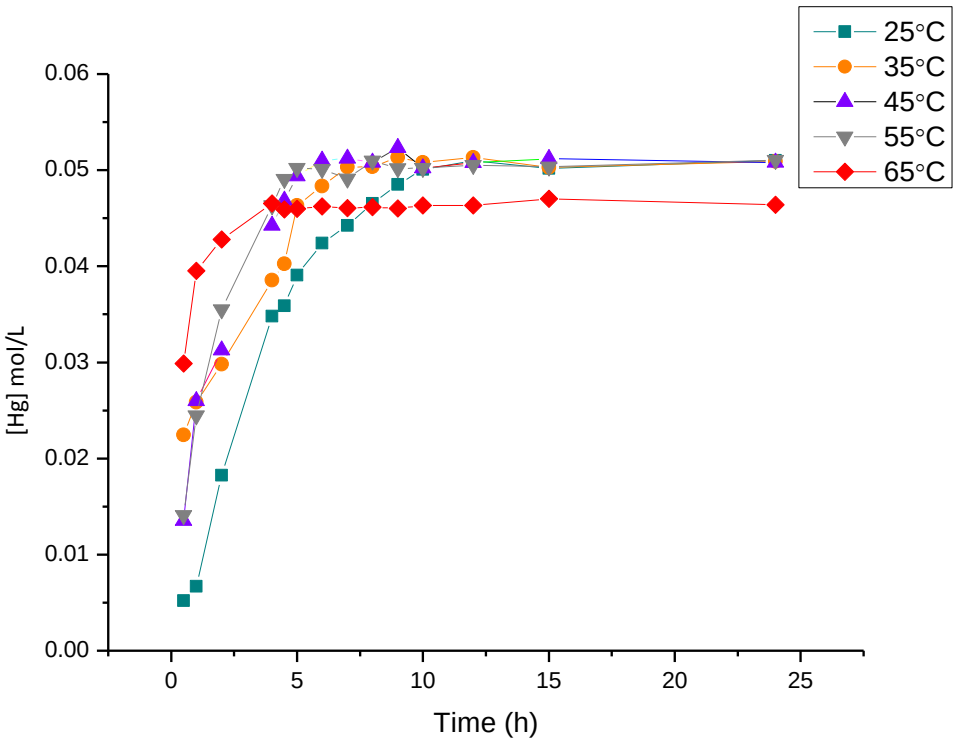


Figure 2- 6 Influence of temperature on dissolution of mercury. 100 mg mercury, 10 ml, 4% w/v concentration of KI/I_2 (0.16/0.053 M), pH 5, 50 rpm stirring. The mercury concentration of 0.05 mol/L corresponds to 100% of available mercury dissolved in these tests.

2.3 Summary of elemental mercury dissolution in I_2/KI solutions

Potassium iodide and iodine solution were studied as an efficient method to dissolve and to achieve decontamination of mercury. It was found that an increase in KI/I_2 solution concentration had a positive impact on the dissolution of elemental mercury. Almost 100 mg mercury can be dissolved in 10 ml 4% (0.053/0.16 M I_2/KI) w/v solution after a contact time of 10 h at room temperature, the soluble mercury concentration after dissolution was 0.050±0.002 M. Ratio of potassium iodide to iodine also played an important role in the dissolution of mercury, when the KI/I_2 ratio is less than 2:1, insoluble precipitates of HgI_2 were formed with a decrease in the percentage of mercury solubilised. The formed and precipitated HgI_2 can be dissolved in aqueous KI solution, demonstrating that an excess of potassium iodide is preferred to avoid generation of precipitates and to shift the equilibrium of oxidised mercury(II) iodide to the water soluble halomercurate(II) anions. In the systems studied here, at a suggested ratio of I_2/KI of 1:3 is needed. Besides, dissolution of mercury in solution can perform better under weak acid and mild condition. Temperature can increase the rate and reduce contact time of dissolution of mercury, however, temperature at or above 65 ºC could result in a loss of iodine and reduce the amount of dissolved mercury content.

Chapter 3

Dissolution of elemental mercury in modified halide salts/iodine solutions

As shown in Chapter 2 that KI/I_2 solution can dissolve elemental mercury effectively with 1:1 of I_2: mercury molar ratio required for complete reaction, and a minimum of 1:2 I_2: I^- ratio required in order to ensure that all Hg (II) produced in the aqueous solution is soluble $[HgI_4]^{2-}$ anionic form rather than generating insoluble HgI_2.

In this chapter, the potential to use other salt solutions (Br^- and Cl^-) as alternative to KI are investigated.

3.1 Experimental

3.1.1 Materials and chemicals

To see whether potassium iodide can be substituted by other halide salts to dissolve iodine in solutions, potassium bromide (99%, Sigma-Aldrich), sodium bromide (99+%, Sigma-Aldrich), potassium chloride (>99.0%, Sigma-Aldrich) and sodium chloride were applied with iodine to investigate their dissolving ability of elemental mercury in these solutions. Other chemicals and instruments used in this part were same with section 2.1.1 and 2.1.2.

3.1.2 The suitable ratio of halogen salts:iodine

The influence of salt/iodine ratio was studied in a similar method that was described in section 2.1.4. The KBr, NaBr, KCl and NaCl were examined as the salt solutions with I_2 as oxidant. A series of solutions were prepared with different iodine:salt ratios varied from 1:3 to 1:13, the details are as shown in table 3-1. The mole of iodine is calculated to correspond with the same mole of mercury (1:1 with Hg^0). The quantity of elemental added in 10 ml solution was 100 mg, solutions was contained in vials, stirred at 50 rpm at room temperature for 24 h. If any precipitated solids were formed, they were removed by filtration using filter paper before mercury analysis from the solutions.

Table 3-1 Data of the amount of halogen salts and iodine at different ratios.

I_2:salt	ratio	solute	g in 100 ml	Moles/liter	Moles in 10 ml	Expected mercury solubility mg (1:1 with I_2)
I_2:KBr	1:3	I_2	1.30	0.051	0.00051	102
		KBr	1.82	0.153	0.00153	
	1:5	I_2	1.30	0.051	0.00051	102
		KBr	3.03	0.255	0.00255	
	1:10	I_2	1.30	0.051	0.00051	102
		KBr	6.07	0.510	0.00510	
	1:11	I_2	1.30	0.051	0.00051	102
		KBr	6.68	0.561	0.00561	
	1:13	I_2	1.30	0.051	0.00051	102
		KBr	7.89	0.663	0.00663	
I_2:NaBr	1:3	I_2	1.28	0.050	0.00050	101
		KBr	1.56	0.150	0.00151	
	1:5	I_2	1.28	0.050	0.00050	101
		KBr	2.59	0.250	0.00252	
	1:10	I_2	1.28	0.050	0.00050	101
		KBr	5.19	0.500	0.00504	
	1:11	I_2	1.28	0.050	0.00050	101
		KBr	5.70	0.550	0.00554	
	1:13	I_2	1.28	0.050	0.00050	101
		KBr	6.74	0.650	0.00655	
I_2:KCl	1:3	I_2	1.27	0.050	0.00050	100
		KCl	1.12	0.150	0.00150	
I_2:NaCl	1:3	I_2	1.27	0.050	0.00050	100
		NaCl	0.88	0.150	0.00150	

3.1.3 Influence of concentration

100 mg (0.5 mmol) elemental mercury was contacted with 10 ml various concentration (as shown in table 3-2) of halide salts and iodine solution for 24 h at room temperature to study the effect of solution concentration on the dissolution of mercury. Stirring speed was 50 rpm. The ratio of I_2 to salts were kept 1:11 and 1:13 for KBr and NaBr respectively.

Table 3- 2 Data of the amount of halogen salts and iodine in different concentrations.

Solution	Concentration w/v	solute	g in 100 ml	Moles/liter	Moles in 10 ml	Expected mercury solubility mg (1:1 with I_2)
KBr/I_2	5%	I_2	0.80	0.0315	0.00031	63
		KBr	4.20	0.3529	0.00353	
	7%	I_2	1.14	0.0448	0.00045	89
		KBr	5.86	0.4928	0.00493	
	8%	I_2	1.30	0.0510	0.00051	102
		KBr	6.70	0.5630	0.00563	
	9%	I_2	1.46	0.0575	0.00057	115
		KBr	7.54	0.6336	0.00634	
	10%	I_2	1.63	0.0640	0.00064	128
		KBr	8.37	0.7034	0.00703	
$NaBr/I_2$	5%	I_2	0.80	0.0315	0.00031	63
		NaBr	4.20	0.4082	0.00408	
	7%	I_2	1.12	0.0440	0.00044	88
		NaBr	5.88	0.0571	0.00057	
	8%	I_2	1.28	0.0504	0.00050	101
		NaBr	6.72	0.6531	0.00653	
	9%	I_2	1.43	0.0563	0.00056	112
		NaBr	7.57	0.7357	0.00736	
	10%	I_2	1.60	0.0630	0.00063	126
		NaBr	8.40	0.8164	0.00816	

3.1.4 Influence of pH

To examine the effect of solution pH on dissolution, the pH of standard solutions of aqueous KBr/I_2 (10 ml each) with overall concentration of 8% w/v (0.051/0.563 M I_2/KBr) were varied by addition of drops of either 0.1 M hydrochloric and 0.1 M potassium hydroxide to adjust the solution pH to 2, 3, 4, 5, 6, 7, 8, 9, 11 respectively. Mercury dissolution tests were then conducted as previously described. 100 mg Hg was contacted with 10 ml solutions over 24 hours at room temperature and 50 rpm.

3.1.5 Influence of temperature

The influence of temperature on the dissolution of mercury in bromide/iodine solution

was studied in a similar way as section 2.1.6. Four vials of 8% w/v potassium bromide and iodine (11:1) solution (10 ml) should be prepared and then heated using a hot plate to adjust the temperature across the range 25-55 ºC. The amount of elemental mercury was 100 mg for each vial.

3.2 Results and discussion

3.2.1 Influence of halogen salt: I_2 ratio

Compared to the potassium iodide/iodine solutions, it was found to be more difficult to dissolve iodine in the bromide and chloride salt solutions: iodine was less soluble in chloride and bromide solution compared to iodide solution with the same condition, and as well as having lower solubility, dissolution of iodine was also slower especially with the chloride salt solutions. Fig. 3-1 shows the difference of iodine soluble ability between in chloride and iodide solution, iodide solution (right) became dark brown colour quickly when added iodine in this solution, however, the colour of chloride solution (left) was lighter and left more solid iodine visibly in solution than iodide solution when added same amount of iodine at the same time.

Figure 3-1 Comparison between solubility of iodine in KCl solution (left) and KI (right)

Replacing the iodide solution with chloride, solutions containing both KCl and NaCl were examined. 100 mg mercury was contacted with 10 ml solutions containing 0.05/0.15 M I_2/KCl or I_2/NaCl solutions, it was found that chloride/I_2 solution performed poorly in the dissolution of elemental mercury as it formed red coloured fine precipitate (as shown in Fig.3-2), this precipitate was α-form HgI_2, which is insoluble in water. Increasing the ratio of chloride: iodine by adding additional potassium chloride or sodium chloride to this solution (Fig.3-2) did not result in redissolution of the HgI_2

precipitate in the chloride solution no matter how much the chloride salt concentration was increased, the final concentration of chloride had been tried of about 2 g/10ml. The concentration of soluble mercury was tested of 0.0017±0.0008 and 0.0023±0.0006mol/L in KCl/I_2 and $NaCl/I_2$ solutions respectively, which indicated a poor effectiveness on dissolution of mercury in chloride solutions.

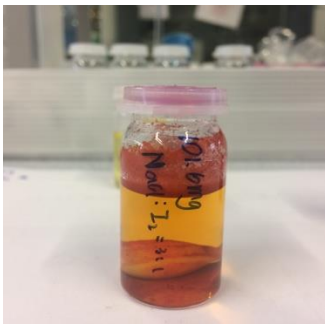


Figure 3-2 Red-coloured fine precipitate in chloride-salt solution

With the bromide salts, sodium bromide and potassium bromide, as shown in figure 3-3, the effectiveness of the bromide/iodine solutions to dissolve mercury was enhanced significantly by increasing the salt:iodine ratio.

For KBr/I_2 system, solutions at ratio below 11:1 produced a red precipitate of HgI_2 (as shown in Fig 3-4). The concentration of mercury in solution increased with an increasing amount of potassium bromide because the insoluble HgI_2 can be dissolved in the bromide solution, or the excess Br^- shifted the HgI_2 equilibrium into soluble $[HgI_2Br_2]^{2-}$. Therefore, until the amount of KBr was added to a ratio of 1:11 (0.051/0.561 M I_2/KBr), all elemental mercury was observed being dissolved as I_2/KBr solution after dissolution was pale yellow, clear and has no precipitate. A mercury concentration of 0.051±0.002 mol/L and 0.050±0.002 mol/L was achieved at I_2: KBr ratio of 1:11 and 1:13 (0.051/0.663 M I_2/KBr) respectively, so the minimum ratio of I_2/KBr in solution needed to generate completely dissolved mercury species was 1:11.

For $NaBr/I_2$ system, the performance on mercury dissolution was similar with

potassium bromide, indicating that changing the cation from K^+ to Na^+ had no significant effect on performance. At ratio of 1:13 (0.05/0.065 M) I_2/NaBr, all the mercury added was observed to have dissolved visibly in the solution, because there was no unreacted mercury or precipitate was left in solutions and mercury concentration after dissolution was tested of 0.051±0.001 mol/L.

As mentioned above, the minimum ratio of potassium iodide to iodine was 2:1. In addition, potassium iodide/iodine solution at ratio of 3:1 (0.053/0.160 M KI/I_2) can convert all elemental mercury into soluble species$^-$ and its mercury concentration was 0.051±0.002 mol/L. However, bromide solutions at 3:1 (0.051/0.153 M KBr/I_2 and 0.050/0.150 M NaBr/I_2) transferred almost elemental mercury to insoluble precipitate HgI_2, its mercury concentration in solutions was 0.0003±0.0020 and 0.0020±0.0002 mol/L for KBr and NaBr solution respectively. Chloride salts and iodine solution performed badly on producing soluble $[HgI_4]^{2-}$. For the purpose of decontamination of mercury and for the next procedure- capture soluble mercury from solutions- can be realized, the high solubility efficiency of mercury in solution was expected in this experiment. According to the solubility of iodine in halide salt solutions, the effectiveness on elemental mercury dissolution in these halogen salts/iodine solutions can be putted in sequence: $I^-/I_2 > Br^-/I_2 > Cl^-/I_2$.

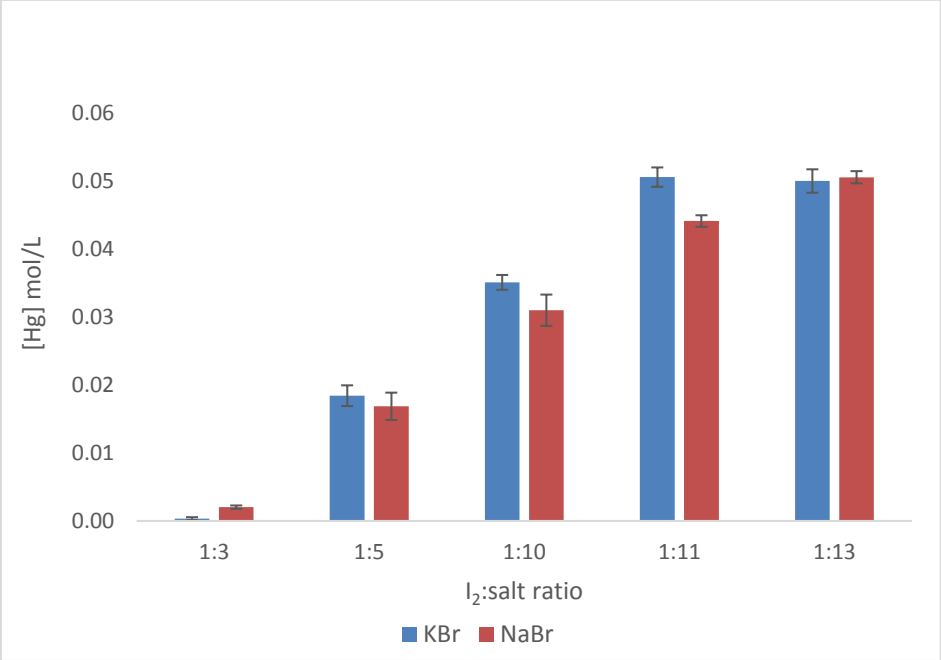


Figure 3- 3 Influence of ratio of potassium bromide and sodium bromide to iodine, 100mg mercury, 10 ml, and concentration for I_2 was same-0.05 M, pH 5, 24 h, room temperature, 50 rpm stirring.

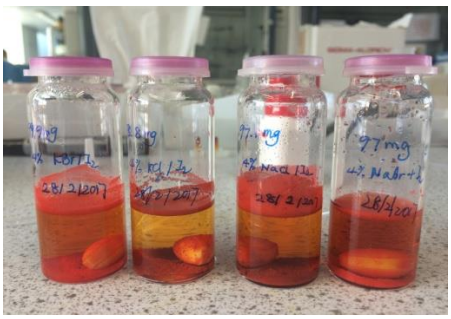


Figure 3-4 Red-coloured precipitate occurred in bromide solution when bromide salts are not enough.

3.2.2 Influence of concentration

The results above show that iodine dissolved in sodium bromide and potassium bromide solutions can dissolve elemental mercury, Fig.3-5 and 3-6 indicated that the concentration of Hg increased with an increasing concentration of bromide/iodine

solution. For both KBr/I_2 and $NaBr/I_2$ solution, the minimum concentration required to oxidise the 100 mg samples of elemental mercury in these experiments (using 10 ml volumes of solution) and to achieve 'complete' dissolution was 8% w/v. At concentrations below 8%, some unreacted elemental mercury was found left in pale-yellow solutions, the concentration of mercury tested for KBr/I_2 solution at 5% and 7% w/v was 0.026±0.001 and 0.046±0.001 mol/L. For $NaBr/I_2$ solution, mercury concentrations of 0.033±0.001 and 0.046±0.002 mol/L were determined for the 5% and 7% w/v, systems respectively. At concentrations above 8%, elemental mercury was considered all dissolved because the concentration of mercury after dissolution maintained in a maximum constant (about 0.05 mol/L) and no unreacted mercury or precipitate was observed to be present in the reaction mixtures. When the solution concentration was 8%, the mercury concentration after 24 h dissolution was 0.051±0.001 and 0.052±0.001 for $NaBr/I_2$ (0.6531/0.0504 M) and KBr/I_2 (0.5630/0.0510 M) systems respectively, corresponding to 101.2±4.1% and 101.4±4.4% mercury dissolution in $NaBr/I_2$ and KBr/I_2 solution respectively.

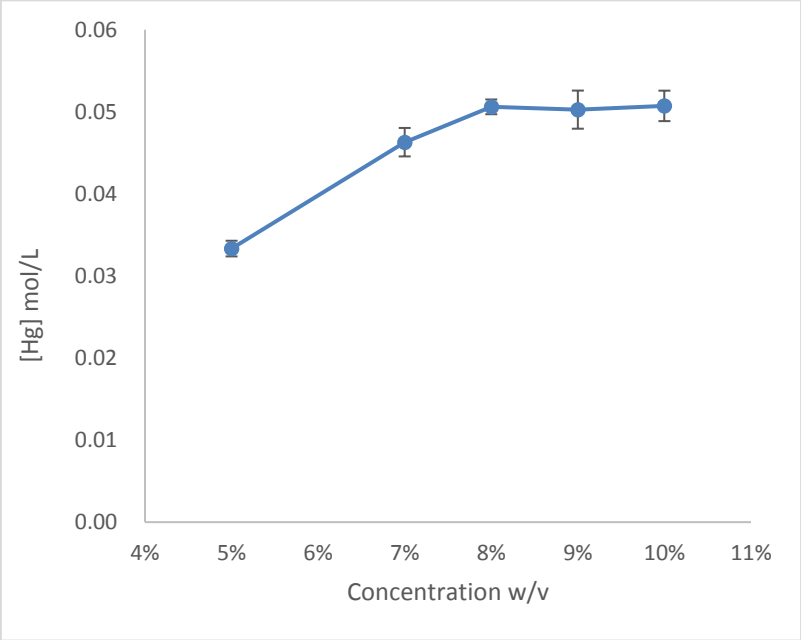


Figure 3-5 Influence of NaBr/I_2 (13:1) concentration on the dissolution of elemental mercury. 100 mg mercury, 10 ml, 24 h, room temperature, pH 5, room temperature, 50 rpm stirring.

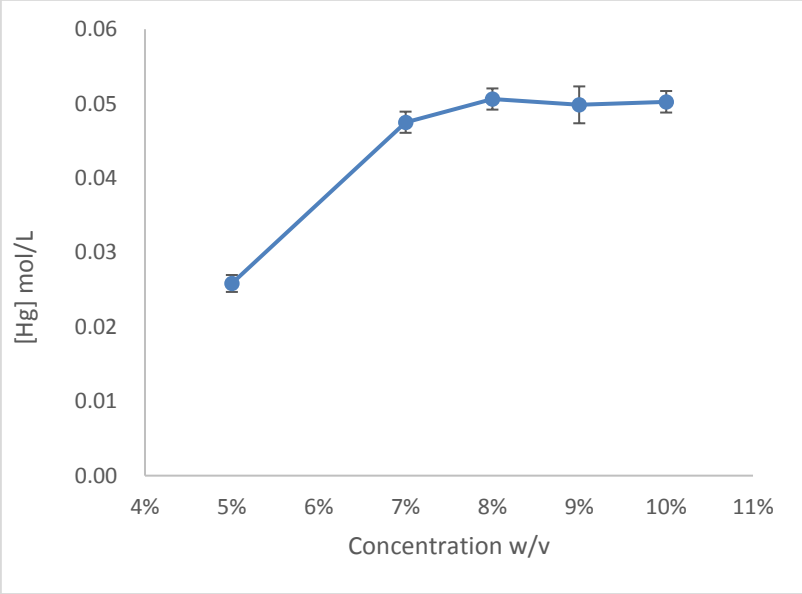


Figure 3-6 Influence of KBr/I_2 (11:1) concentration on the dissolution of elemental mercury. 100mg mercury, 10 ml, 24 h, room temperature, pH 5, room temperature, 50 rpm stirring.

3.2.3 Influence of pH

The impact of pH on mercury dissolution in potassium bromide/iodine solution was examined in the range from 2 to 11. The results are shown in Fig.3-7, it's efficient to achieve a complete dissolution of mercury for bromide/iodine solution under acid and neutral condition, the dark brown solution turned to pale yellow and there was no elemental mercury or precipitate left in solutions after a 24 h contact. The dissolved mercury concentration decreased with a rise of pH when pH was above 7, some unreacted elemental mercury could be observed left in solutions, the dissolved Hg concentration was 0.043±0.001, 0.034±0.002 and 0.026±0.001 mol/L when the pH of solution was 8, 9 and 11 respectively.

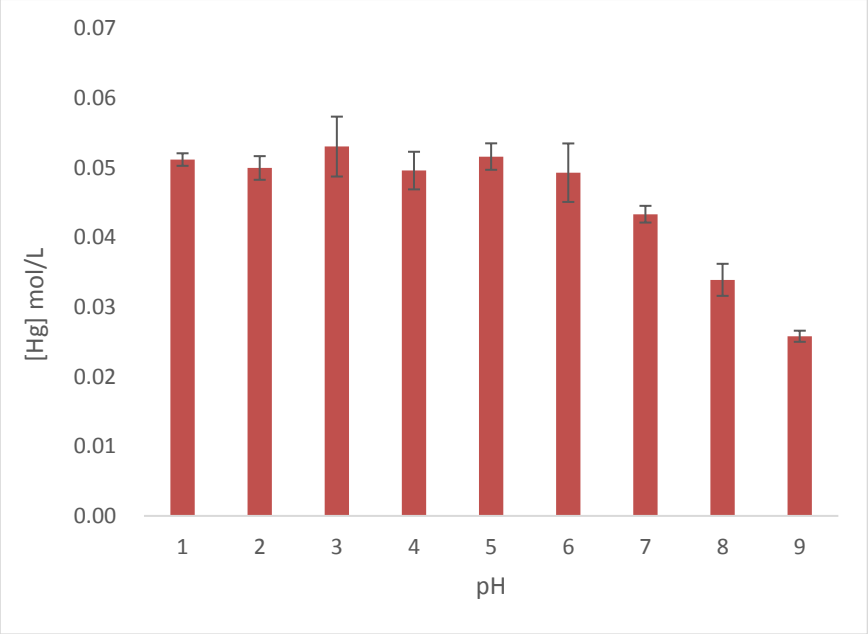


Figure 3-7 Influence of pH on dissolution of mercury in KBr/I_2 solution. 100 mg mercury, 10 ml, 8% w/v concentration of KBr/I_2 (0.0510/0.5630 M I_2/KBr) solution, 24 h, room temperature 50 rpm stirring.

3.2.3 Influence of temperature

The effect of temperature on the dissolution of mercury in bromide/iodine solution was

investigated and the results are shown in Fig.3-8. The rate of mercury dissolution was more rapid at higher temperatures, but the extent of increase is less significant than had been observed for the potassium iodide/iodine solutions. At room temperature, the dissolved mercury concentration increased with time over 10 h, at which point there was no unreacted elemental mercury left in solutions and the concentration of mercury in solution was constant at 0.05 mol/L (corresponding to complete dissolution). When the temperature was increased to 45 ºC, the concentration of mercury reached the maximum value after 7~8 h, showing an increase in dissolution rate. However, it occurred some unreacted elemental mercury left in solutions at the higher temperature (55 ºC), the concentration of dissolved mercury was 0.035±0.001 mol/L at 10 h, it may because of the loss of iodine due to the sublimation at high temperature which appear to be more pronounced than in the iodide/iodine system. The exist of I^- can reduce the evaporation of I_2 due to the formation of stable I_3^-, however Cl^- is investigated that has no inhibition effect on iodine evaporation from solutions [75, 77]. The properties of bromide tend to be intermediate between chloride and iodide. It can be explained why it appeared iodine loss at 65 ºC in iodide solution but at 55 ºC in bromide solution, and the extent of I_2 evaporation in bromide solution is bigger than in iodide solution, the final concentration of dissolved mercury at 65 ºC for I^-/I_2 solution was 0.046±0.002 mol/L.

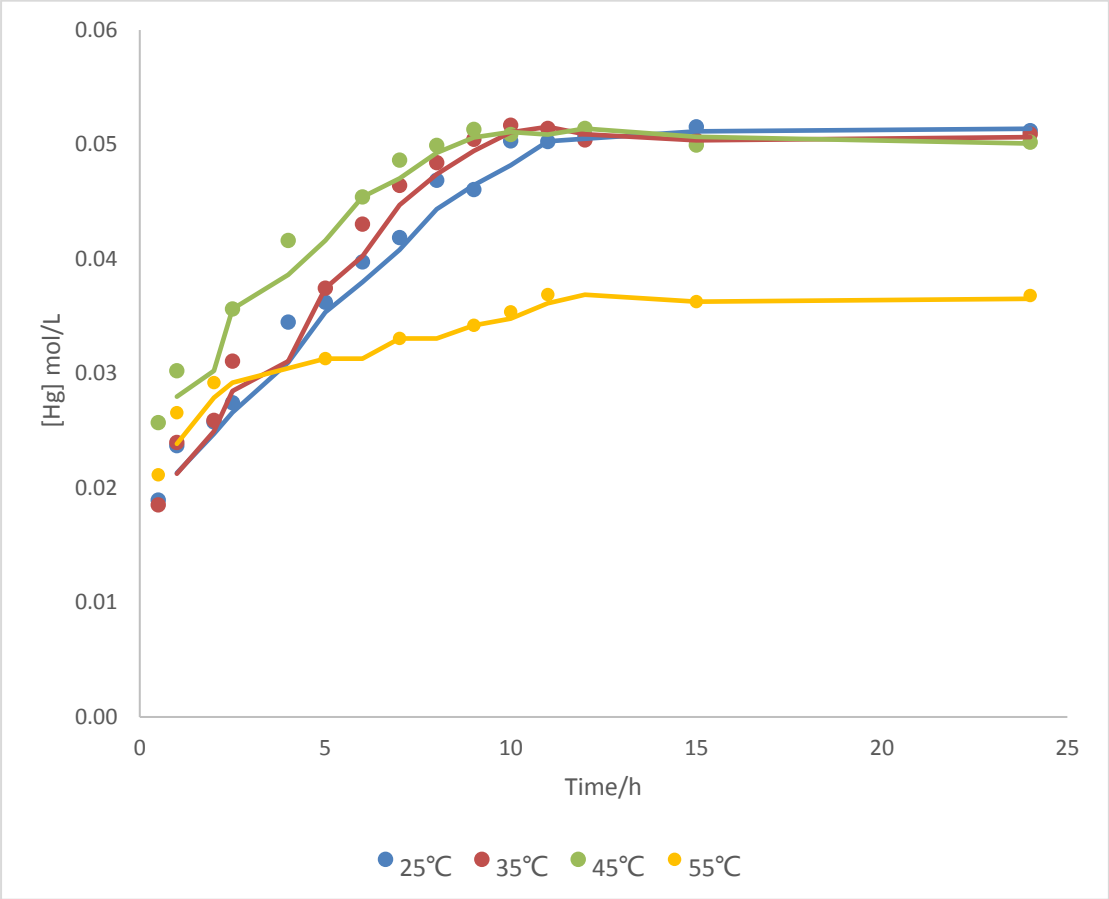


Figure 3-8 Influence of temperature on mercury dissolution in potassium bromide and iodine solution. 100 mg mercury, 10 ml, 8% w/v concentration of KBr/I_2 (0.5630/0.051 M), pH 5, 50 rpm stirring. The mercury concentration of 0.05 mol/L corresponds to 100% of available mercury dissolved in these tests.

3.3 Summary of elemental mercury dissolution in modified halide salt/iodine solution

The bromide/iodine solution had an ability to dissolve elemental mercury when a high ratio of salt to iodine is used, because it's harder for iodine to dissolve in bromide solution than in iodide solution. HgI_2 was shown to be soluble in bromide solutions. However, the Cl^-/I_2 systems performed badly in the dissolution of mercury because it can only convert elemental mercury to insoluble precipitate rather than soluble mercury complexes in solutions. Table 3-3 shows a comparison of the effectiveness of the KI, KBr and NaBr systems for dissolution of mercury. The minimum concentration of potassium iodide, sodium bromide and potassium bromide to dissolve 100 mg mercury in 10 ml solution could be 4%, 8%, 8% w/v (g/ml) respectively. Obviously, it cost more amount of bromide salt to dissolve the same quantity of elemental mercury and iodine than potassium iodide. The calculated equilibrium constant Kc at room temperature of KI/I_2 was 1.96, bigger than it of KBr (0.16) and NaBr (0.12), it can be concluded that I^-/I_2 solution is more effective than Br^-/I_2 solution for the dissolution of mercury. There were no significant differences in the ability to dissolve mercury between KBr and NaBr with iodine solution, however, consider the price of KBr and NaBr and the cost of process, KBr (143.5 GBP/kg) is cheaper than NaBr (368 GBP/kg) [78, 79], KBr/I_2 is more recommended for application here.

Table 3-3 Comparison between halide salt/iodine solutions on the dissolution of elemental mercury

Solution	Concentration w/v	Ratio of salt:I2	Concentration of salt/I2 (M)	Mercury concentration after dissolution (M)	Equilibrium constant Kc Litre/mole
KI/I2	4%	3:1	0.160/0.053	0.050±0.002	1.96
KBr/I2	8%	11:1	0.563/0.051	0.051±0.001	0.16
NaBr/I2	8%	13:1	0.653/0.050	0.051±0.001	0.12

Chapter 4

Extraction and capture of leachate mercury from solution

4.1 Experimental

4.1.1 Materials and instruments

As discussed in the introduction, a further procedure of extracting mercury from water is needed after dissolution of mercury to avoid additional contamination. Precipitation and ion exchange are two effective methods to capture mercury from aqueous solution. Precipitation is a treatment that forms insoluble solid by using specific chemicals to mix with dissolved contaminants (heavy metals) and then separate the solid from wastewater. For mercury, these chemicals could be 2,4,6-Trimercapto-s-triazine, tri-sodium salt (TMT), potassium/sodium thiocarbonate (STC), sodium dimethyldithiocarbamate (SDTC) and other thiol-organic chemicals. However, STC was reported that it produces a volatile and toxic carbon disulfide by-product when it is precipitated with metals. SDTC was also investigated that it has a decomposition tendency of mercury-SDTC ligand and formed toxic secondary compounds [56]. TMT-15 is widely used for mercury control in waste water treatment in incineration plants (domestic waste, biomass, refuse derivated fuel), coal fired power stations, and for flue gas scrubbing and condense water treatment because it forms stable insoluble metal-TMT complexes and doesn't produce dangerous compounds. Purolite S924 and S920 are reported as a high mercury selective resin with a minimum mercury adsorption capacity of 200 g/L [68, 71] and are used as high selectivity, high capacity adsorbents for mercury removal in wastewaters to meet mercury discharge limits. Therefore, two commercial treatments were selected to remove soluble mercury (Hg^{2+}) from solutions: precipitate with TMT-15 (98%, Evonik), ion exchange for adsorption using Purolite S920 and S924 mercury selective resin.

The mercury-containing solutions (10 ml) were acquired from chapter 2 -the KI/I_2 solution after dissolving mercury: the concentration of mercury was about 0.05 mol/L (10 g/L), the initial pH of mercury-containing solution was about 7~8.

For pH adjusting, using either hydrochloric acid (34%, Sigma-Aldrich) or sodium hydroxide or potassium hydroxide (Sigma-Aldrich).

4.1.2 Influence of dose

A. TMT-15

TMT-15 is a 15% aqueous solution of 1,3,5-triazine-2,4,6-trithiol tri-sodium salt, the molecular weight of TMT is 243.22 g/mol and the density of TMT-15 is 1.12 g/ml [80]. The sodium salt reacts with the mercury ions in the aqueous solution to form a stable and insoluble precipitate. TMT-15 bond with mercury by the formation of a coordination polymer containing mercury ions bound through strong bond with two S atoms. The N atom in the triazine ring provides lone pair electrons and form coordination bonds with mercury ions. Mercury ions are coordinated with two S and N atoms to form insoluble compounds (Hg-TMT), which has stable chelate rings [59]. Fig.4-1 is the schematic of Hg-TMT compounds after coordination.

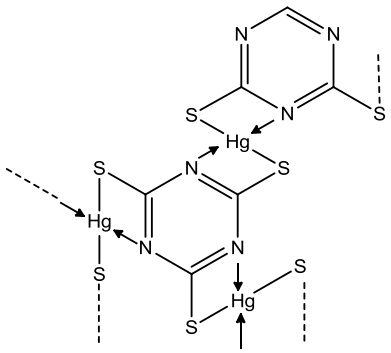


Figure 4-1 Structure of Hg-TMT complexes

According to the known concentration of mercury (0.05 M) and equation (5) of the reaction between TMT and mercury, the stoichiometric amount of TMT-15 can be calculated of 0.54 g.

$$3Hg^{2+} + 2TMT^{3-} \rightarrow Hg_3TMT_2 \downarrow \quad (5)$$

A series of 10 ml solutions containing mercury(II) were prepared and TMT-15 added to each in varying amounts: 20% molar deficit (0.8 equivalents, based on equation (5) above), 10% molar deficit, stoichiometric, 10% molar excess, 20% molar excess, 30% molar excess, 50% molar excess, 60% molar excess, 70% molar excess (as shown in table 4-1). Samples were stirred with a magnetic stirrer at 50 rpm for 4 hours at room temperature and the precipitate of mercury-TMT complex formed was filtered through a cotton wool plug. A 10 µL aliquot of the clear filtered solution was taken, diluted in the same way as described in section 2.1,2, and the residual mercury content was measured using the DMA-80 mercury analyser. For subsequent calculation of the residual mercury concentration, the volume of the TMT-15 aqueous solution has to be included into the analysis.

Table 4- 1 Data of TMT-15 amount in different dosage.

TMT-15 Dose	TMT-15 amount/g	volume/ml	TMT molar	stoichiometric mass of mercury (3:2 with TMT) in 10 ml, mg
-20%	0.43	0.39	0.00027	80
-10%	0.49	0.43	0.00030	90
stoichiometric	0.54	0.48	0.00033	100
+10%	0.59	0.53	0.00037	110
+20%	0.65	0.58	0.00040	121
+30%	0.70	0.62	0.00043	130
+50%	0.81	0.72	0.00050	150
+60%	0.86	0.77	0.00053	160
+70%	0.92	0.82	0.00057	170

B. Resin S924, S920

A series of 10 ml Hg(II)-containing (1000 ppm) solution were prepared and Purolite S924 resin added to each in different amounts varied from 0.04 g to 0.1 g. All these samples were presented in vial and were stirred with a magnetic stirrer at 50 rpm for 15 hours at room temperature. The spherical resin particle was filtered through a cotton wool plug and got clear solution that diluted in the same way as described in section 2.1.2. The residual mercury content was measured using DMA-80 mercury analyser.

Do the same procedures to S920 with the dosage range from of 0.05 to 0.1 g.

4.1.3 Influence of initial mercury concentration

A. TMT-15

TMT-15 solutions were added to a series of 10 ml solutions containing mercury(II) at 10000, 7000, 5000, 3000, 1000 ppm concentration. The volume of TMT-15 solution added was varied to maintain a constant, stoichiometric molar ratio to the mercury content (3:2 of Hg^{2+}: TMT). Samples were stirred at room temperature at 50 rpm for 5 hours then filtered, and prepared for analysis as described in section 4.1.2.

B. Resin S924, S920

In order to observe the influence of initial Hg concentration on the mercury capture, 10 ml Hg-containing solutions with the initial concentration that were varied from 20 to 1000 (20, 50, 100, 200, 500, 650, 800, 1000) ppm were each prepared to mix with 0.07g S924 or 0.08g S920. Each sample were conducted in a vial with a magnetic stirrer at 50 rpm for 15 hours at room temperature.

4.1.4 Influence of pH

Diluted the 10000 ppm mercury leachate solution into 1000 ppm

A. TMT-15

Prepared 8 vials of 10 ml 1000 ppm mercury solution to adjust its pH to 2,3,4,5,6,7,8,9,10 respectively, and then added 30% molar excess TMT-15 into the solution, stirred at 50 rpm and room temperature. For each pH solution, took samples from solution at 15 minutes, 30 minutes, 1 hour and 4 hours to test its mercury content. In order to avoid change the total volume of solution, the volume of sample that was taken from solutions at each time point should be as small as possible (100~200 μL). For each sample, it can be filtered by injecting into a pipette, which filled by cotton.

B. Resin S924, S920

Use 8 vials to hold 10 ml of mercury solution with Hg concentration of 1000 ppm, which have been adjusted pH to 2, 3, 4, 5, 7, 8, 9, 11 respectively, then add the same dosage of resin S924 of 0.07 g for each. These samples were suggested to be kept on a stir plate for 15 hours at 50 rpm to reach the equilibrium condition. The way of pH test for S920 was same with S924, but the dosage of S920 was 0.08 g.

4.1.5 Influence of temperature (Resin)

To determine the influence of temperature on the adsorption of mercury by resin, three temperatures were considered: room temperature (25 ºC), 35 ºC, and 45 ºC. 10 ml Hg-containing (1000 ppm) solution were contacted with 0.07 g Purolite S924 or 0.08 g Purolite S920 resin in a vial with a stirring speed of 50 rpm for each temperature. The mercury concentration was tested during a series of time point from 10 min to 24 h. In order to maintain the same volume-mass ratio as a constant, the

volume of samples for each time point should be taken care, in this experiment, took 1μL out from solution for the test in DMA-80.

4.2 Results and discussion

4.2.1 Effectiveness of TMT-15 on removing mercury from solution

4.2.1.1 Effect of TMT-15 dose

On addition of TMT-15 solutions to the mercury(II)-containing ($[HgI_4]^{2-}$, 0.05 M) test samples, a grey-coloured dense precipitate formed immediately. These precipitates are the virtually insoluble mercury-TMT complex that is easy to separate by filtration [57]. An increase in the removal efficiency of mercury was achieved when the TMT-15 dosage was increased, shown in Fig.4-2. The residual mercury concentration was reduced from 1.238±0.194 g/L to 0.028±0.025 g/L when the dosage of TMT-15 was increased from -20% (0.4324 g) to +30% (0.7027 g). Using a TMT-15 dose above 0.07027 g (+30%) resulted in high removal efficiency (>99%) and produced aqueous solutions that were colourless and clear after filtration. The residual mercury concentrations obtained with different TMT-15 dosages were 0.028±0.025, 0.026±0.027, 0.025±0.020, 0.002±0.021 g/L at TMT-15 dosage of +30%, +50%, +60%, +70%, respectively. So in this case, dosage of TMT-15 at 0.7027 g was sufficient and effective to remove more than 99% soluble mercury from 10 ml solutions of initial mercury concentration of 10 g/L.

The removal efficiency found here is higher than have previously been reported by Matlock [56] who used TMT-15 to capture mercury and achieved a removal efficiency of 79% with a final concentration of mercury of 10.5 ppm. The EPA report that the discharge limit of mercury is 0.2 ppm for water in the US [56]. The residual concentration of mercury found in these screening tests was 2-20 ppm, higher than

this limit. However, there are a number of reasons that should not restrict further development and applications. First, the relatively large residual mercury concentrations in solution may due to the high initial concentration of mercury. It may need a second “polishing” treatment such as ion exchange or adsorption to remove mercury to achieve the discharge limitation. Fulbright et al. [81] used ethyl acetate to extract $HgCl_2$ from wastewater produced by chlor-alkali plant, it needed 2 extraction stages for initial mercury concentration of 500 ppm, but 3 more extraction stages were needed for removing mercury with initial concentration of 20000 ppm due to the second procedure of activated carbon adsorption. Second, Laboratory scale of chemical precipitation may less efficient than large scale [82]. Hensman [83] used a thiol-containing organic complexing agent (OTC) to remove mercury from 200 ppb to 0.02-0.5 ppb in a bench test, and expand the batch-flow system to the continue-flow pilot plant, Hg concentration then can be controlled below the detectable limits of 0.2 ppt of Hg. A natural gas production site in Thailand reduced mercury concentration from 9600 ppb to 0,035 ppb by using thiol-based agent in full scale [37].

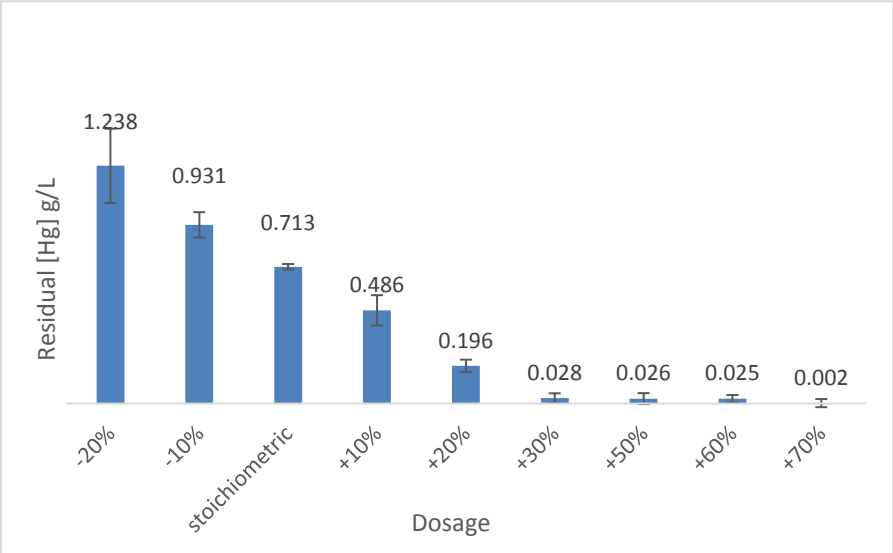


Figure 4-2 Effect of TMT-15 dosage. 10000 ppm mercury solution, 10 ml, room temperature, 4 h, pH 8, 50 rpm stirring. The error is standard deviation from triplicate measurements.

4.2.1.2 Effect of contact time

Because TMT-15 was effective using a 30% molar excess dosage to achieve good mercury removal, this system was used to then investigate the effects of mixing and contact time. Figure 4-3 shows mercury removal from solution after addition of TMT-15 as a function of contact time before separation. The initial solutions contain mercury(II) ions at 10000 ppm concentration and with 1 h contact time, the removal efficiency and residual mercury concentration were achieved of 99.65±0.20% and 0.028±0.025 g/L at 1 h. In addition, the removal efficiency was nearly constant at over 99% after longer contact times, which indicated Mercury-TMT complexes were chemically stable and insoluble, there was no obvious decomposition of mercury-TMT complexes and increase of residual mercury concentration over time. It's reported that Mercury-TMT complexes are very stable and only possibly can be cracked completely by contacted with aqua regia under 180 °C for 4 h, what's more, Mercury-TMT precipitate is thermally stable up to 250°C [57]. Matlock compared heavy metals removal from solutions using TMT, STC and SDTC with an initial mercury concentration of 50 ppm. It was found that final mercury concentrations of 15.15, 16.90, and 10.50 ppm were achieved after 1, 6, and 20 h respectively using a 10% excess of TMT. In contrast, with STC, some metal concentrations increased over time due to the formation of soluble Hg-ligand complexes or decomposition of the metal-ligand complexes [56].

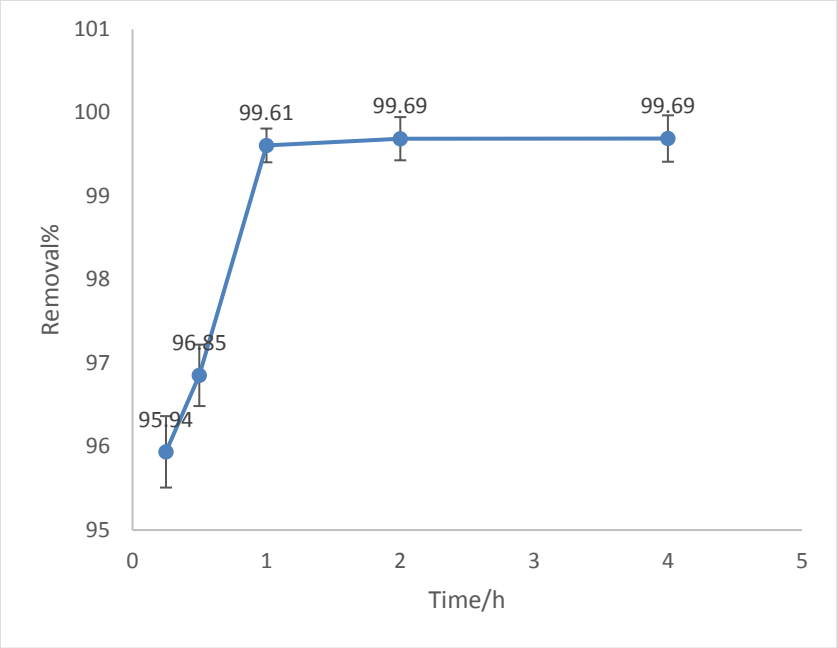


Figure 4- 3 Contact time for TMT-15 with mercury solution. +30% TMT-15 dose, 10 ml, 10000 ppm, room temperature, pH 8, 50 rpm stirring. The error is standard deviation from triplicate measurements.

4.2.1.2 Effect of mercury concentration

The influence of initial Hg concentration on the precipitation of mercury from aqueous solution are illustrated in Fig.4-4. For solutions with initial mercury ion concentrations of 5000 ppm or lower, treatment with TMT-15 resulted in efficient precipitation of mercury-TMT complexes leaving residual Hg concentration in solution between 7.41±6.32 and 28.61±7.54 ppm (Fig. 4-4).

When the initial mercury concentration in solution was higher (7000 and 10000 ppm in Fig. 4-4), incomplete removal of mercury from solution was observed. From the 10000ppm initial solution, the residual mercury concentration after treatment and filtration was 705.13±28.76 ppm which corresponds to a 7% remaining in solution. For initial Hg concentrations lower than 500 ppm, it was found that the small amount of TMT-Hg precipitate formed was suspended in solutions and did not precipitate. Furthermore, the particle size was very small making efficient filtration and removal

impossible. That may because the low level of mercury content is not enough to form large enough chelating flocculants, which are easy to collect and separate by filtration. Some previous study suggested that chemical precipitation is more effective to treat wastewater that has relatively high concentration of toxic metals (>100 ppm) [67].

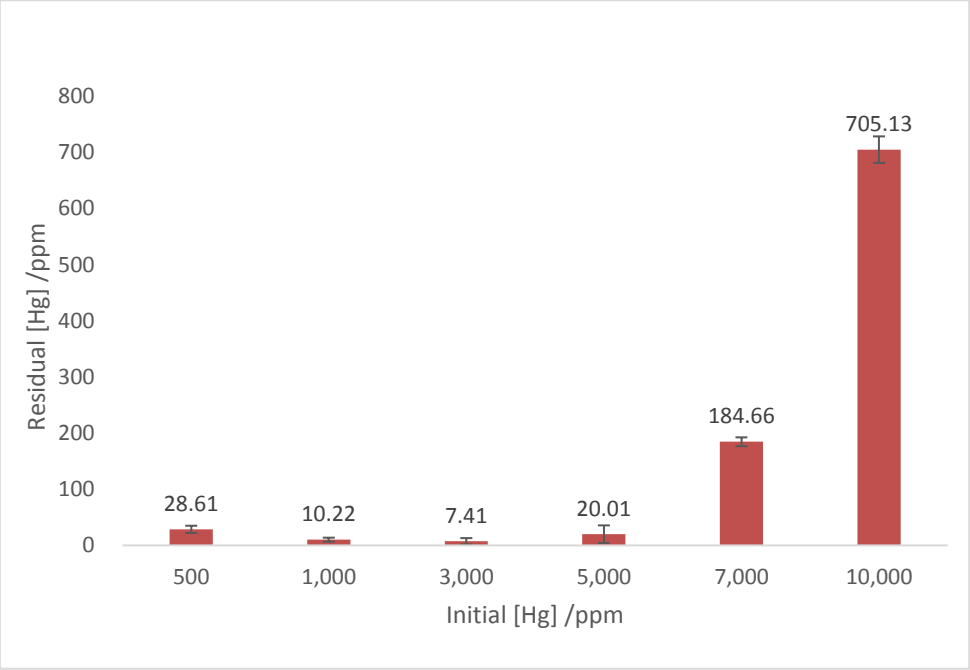


Figure 4- 4 Effect of mercury concentration on the capture with TMT-15. The dosage of TMT-15 is 0.54 g, 10 ml, room temperature, 1 h, pH 8, 50 rpm stirring. The error is standard deviation from triplicate measurements.

4.2.1.3 Effect of pH

TMT-15 is reported to be effective as a mercury precipitant over a wide pH range in both alkaline and acid environments [57]. Results from extraction over a range of pH between 3-10, treating mercury-containing (1 g/L) solutions with 30% molar excess TMT-15 are shown in table 4-2. This data confirms that Mercury-TMT complexes are stable over this pH range as the residual mercury concentration didn't increase too much over time. Fig.4-5 shows data for 0.5 h contact times (from table 4-2, residual

mercury concentration versus pH). TMT-15 was effective over a wide pH range, the removal efficiency was over 90% at pH 4-10. TMT-15 performed better under alkaline conditions, the residual mercury concentration in solutions was 0.025±0.026, 0.012±0.018, 0.032±0.033 g/L at pH value of 8, 9, and 10 respectively. For better mercury precipitation, alkaline condition is more stable and preferred, because the increased H^+ might has a competition with Hg^{2+} to bond with S atom at low pH, and thiols rather than thiolate (-SH rather than $–S^-$) groups are less strongly coordinating to Hg^{2+} and would reduce the number of ligating sites involved in the chelating reaction. Besides, the reason why TMT-15 can remove mercury more efficiently at alkaline condition is the formation of hydroxide coagulant or flocculants, which have a good capture effect on mercury [59].

The final mercury concentration reduced from 147.7 mg/L to 11.5 mg/L when the pH of solution decreased from 3 to 9. Similar results were studied by Matlock et al. [84], who investigated the effectiveness of TMT to extract cadmium (0.088 M) or zinc (0.139 M) from solutions. It found that it was more effective for TMT to extract metals from solutions under alkaline conditions, the final concentration of cadmium was reduced from 31.0 mg/L to 0.07 mg/L when initial pH of solution was increased from 3 to 9, and the final concentration of zinc decreased from 116 mg/L to 4.46 mg/L.

Table 4-2 Results of TMT-15 at different solution pH. The dosage of TMT-15 is 30% molar excess. The error is standard deviation of a triplicate test.

Chelating agent	pH	Time/h	Initial Hg concentration (g/L)	Residual Hg concentration (g/L)	Removal efficiency%
TMT-15	2	0.25	1	0.5779±0.0284	55.23±2.20
		0.5	1	0.3007±0.0136	76.71±1.05
		1	1	0.3465±0.0388	73.15±3.01
		4	1	0.2065±0.0366	84.00±2.83
TMT-15	3	0.25	1	0.2200±0.0184	82.96±1.43
		0.5	1	0.1477±0.064	88.55±0.50
		1	1	0.1300±0.0167	89.93±1.29
		4	1	0.1530±0.0150	88.15±1.17

Chelating agent	pH	Time/h	Initial Hg concentration (g/L)	Residual Hg concentration (g/L)	Removal efficiency%
TMT-15	4	0.25	1	0.242±0.002	81.25±0.17
		0.5	1	0.125±0.041	90.33±3.17
		1	1	0.135±0.010	89.58±0.78
		4	1	0.129±0.063	90.02±4,90
TMT-15	5	0.25	1	0.235±0.019	87.18±1.46
		0.5	1	0.095±0.032	92.64±2.48
		1	1	0.107±0.048	91.68±3.73
		4	1	0.088±0.029	93.44±2.22
TMT-15	6	0.25	1	0.194±0.036	84.95±2.79
		0.5	1	0.090±0.022	93.01±1.70
		1	1	0.063±0.026	95.11±1.99
		4	1	0.109±0.011	92.19±0.84
TMT-15	7	0.25	1	0.146±0.018	88.69±1.42
		0.5	1	0.075±0.028	94.21±0.20
		1	1	0.086±0.019	93.34±1.46
		4	1	0.078±0.003	94.06±0.20
TMT-15	8	0.25	1	0.160±0.013	87.63±1.02
		0.5	1	0.025±0.026	98.10±2.01
		1	1	0.021±0.009	98.41±0.71
		4	1	0.042±0.023	96.71±1.76
TMT-15	9	0.25	1	0.090±0.012	93.03±0.94
		0.5	1	0.012±0.018	99.11±1.36
		1	1	0.0182±0.027	98.60±2.09
		4	1	0.040±0.036	98.89±2.76
TMT-15	10	0.25	1	0.139±0.017	89.71±1.28
		0.5	1	0.032±0.036	97.50±2.52
		1	1	0.050±0.025	96.09±1.93
		4	1	0.039±0.035	96.94±2.74

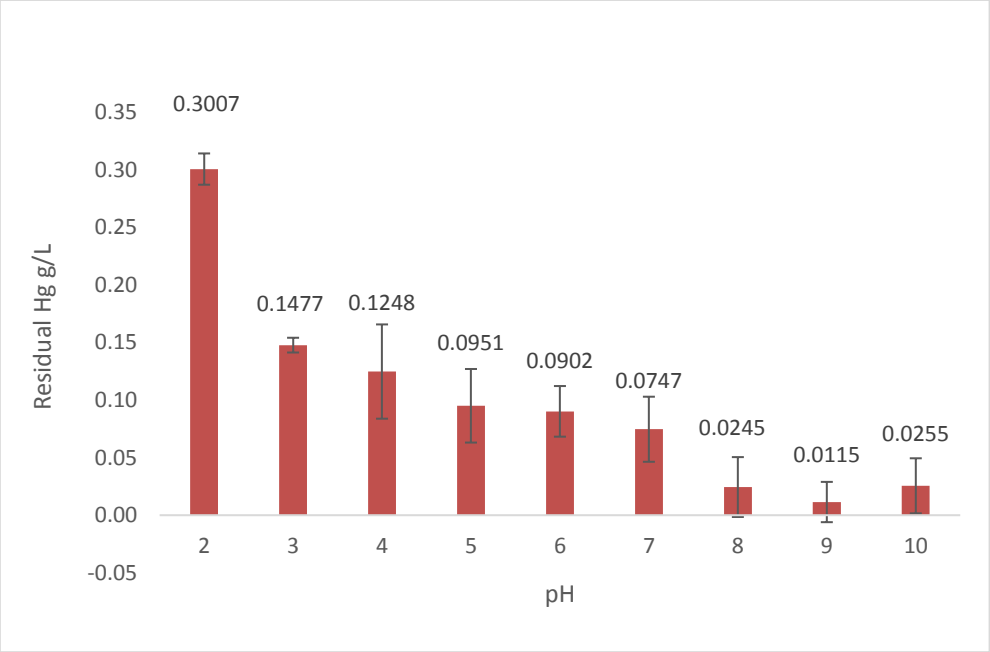


Figure 4- 5 Effect of solution pH on mercury precipitation with TMT-15 at 0.5 h. 30% molar excess TMT-15 dose, 10 ml solution of 1000 ppm (1g/l), 10 ml, room temperature, 0.5 h, 50 rpm stirring. The error is standard deviation from triplicate measurements.

4.2.1.4 Summary of effectiveness of TMT-15

TMT-15 was effective and quick to extract mercury from solution (10000 ppm) within 1 h when added with a 30% molar excess, the residual Hg concentration after removal was 0.028±0.025 g/L. The Hg-TMT complexes are stable and not harmful. Mercury concentration can influence the removal efficiency which was most effective at lower concentrations. However, when the initial concentration of mercury used was below 500 ppm, flocculation and filtration of the fine Hg-TMT complexes proved difficult to achieve and careful processes for efficient filtration would be needed. TMT-15 is effective over a wide pH. It is suggested that the solution pH is adjusted to alkaline conditions in order to make sure precipitate is most insoluble and to achieve a highest removal efficiency.

4.2.2 Ion exchange using Purolite S924 and S920 resin

The sulphur-containing resin Purolite S924 and S920 are chelating polystyrene based resins designed for the selective removal of mercury [68, 71] and are used for capture mercury for wastewater treatment. The adsorption capacity can be calculated by equation (6) or (7):

$$q_e = \frac{C_i - C_e}{W} V \quad (6)\ [85]$$

$$q_e = \text{Removal} \times V \times \frac{C_i}{W} \quad (7)$$

Where q_e is the amount of mercury adsorbed (milligrams per gram); Ci is the initial mercury concentration; C_e is the equilibrium mercury concentration (grams per litre); V is the volume of solution (litres); W is the weight of resin (grams).

4.2.2.1 Impact of resin dosage

A visible colour change was observed in less than 10 min when mercury solutions were contacted with S920 resin: the yellow or orange mercury-containing from KI/I_2 based solutions turned to lighter or colourless., it might because the coloured Hg-containing compounds (iodomercurate) have been adsorbed by Purolite S920 resin. The dosage of S924 or S920 highly influenced the efficiency of mercury adsorption as illustrated in Fig.4-6 and Fig.4-7. It can be observed that the more amount of resin added, the higher mercury removal efficiency achieved. A high-level mercury removal efficiency of 84.28±0.71% and 99.16±1.91% was obtained when solutions contacted with 0.07 g S924 and 0.08 g S920 respectively. Purolite S920 has a higher Hg removal efficiency than S924, this may due to the chelating thiouronium functional groups of S920, which contains both nitrogen and sulphur atoms that can bond with mercury, whereas S924 resin only contains a thiol [67].

However, the adsorption capacity did not increase linearly with the amount of resin

used. Fig.4-6 and Fig.4-7 show that there is an optimal loading of the resin (shown in g resin per 10 ml of solution) for peak mercury removal. The mercury adsorption capacity using 0.06 g S924 was highest at 125.99±3.51 mg/g, then it decreased with an increase of resin dosage. Similarly, the highest value of mercury capacity was 123.81±2.7 mg/g at S920 dosage of 0.08 g. The phenomenon of decreasing adsorption capacity with increased dosage can attribute to the splitting effect of flux between the adsorbents [4], As the increasing of dosage, the ratio of volume-mass (10 ml solution) decreased and then the adsorption capacity may decrease based on the equation (6). For resin Purolite S924 and S920, the optimal dosage to remove mercury from 10 ml mercury-containing solution of 1000 ppm were 0.07 g and 0.08 g respectively.

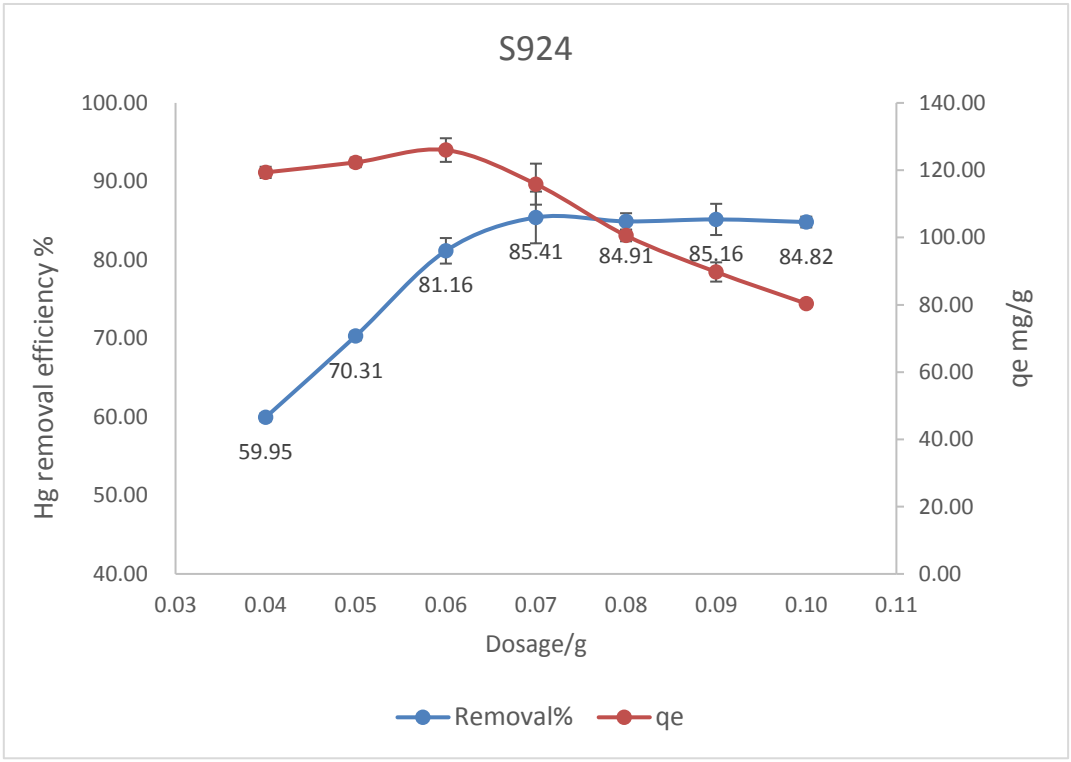


Figure 4-6 Impact of S924 dosage, 10 ml mercury containing solution of 1000 ppm, pH 7, 15 h, and room temperature, 50 rpm stirring. The error is standard deviation from triplicate measurements.

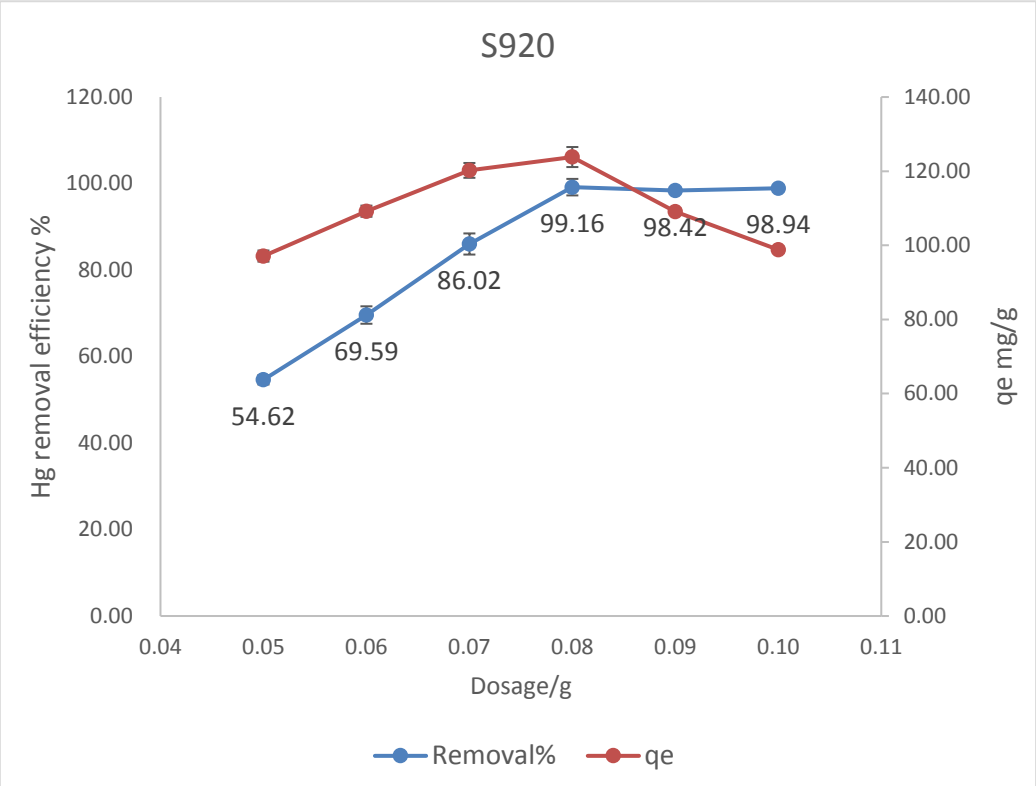


Figure 4- 7 Impact of S920 dosage, 10 ml mercury containing solution of 1000 ppm, pH 7, 15 h, and room temperature, 50 rpm stirring. The error is standard deviation from triplicate measurements.

4.2.2.2 Impact of initial mercury concentration

The impact of initial mercury concentration on the adsorption capacity and equilibrium concentration is shown in Fig.4-8 and Fig.4-9. The Hg adsorption capacity increased with an increasing concentration of initial Hg, whereas the mercury removal efficiency decreased due to the increase of equilibrium Hg concentration. Based on equation (6), when the ratio of solid mass/liquid volume is a constant, an increasing initial mercury concentration leads indeed to an increasing driving force, the concentration gradient [85]. The final mercury concentration achieved in solutions were 0.048±0.002 ppm and 0.076±0.006 ppm when the Hg-containing solution of initial concentration of 20 ppm was contacted with 0.08 g Purolite S920 and 0.07 g S924 respectively. The final concentrations of mercury in solution obtained when the initial Hg concentration was

1000 ppm were 21.273±1.734 ppm (S920) and 203.339±10.302 ppm (S924). The continual increase in mercury adsorption indicates that the resins have not reached their saturation capacities at any stage during the experiments, and so are mass-transport limited.

Some similar results showing that ion exchange resins are effective to treat Hg-containing solutions at very low concentrations [66]. Purolite S920 resin is recommended to treat wastewater of Hg concentration under 100 ppm due to the higher removal efficiency [67].

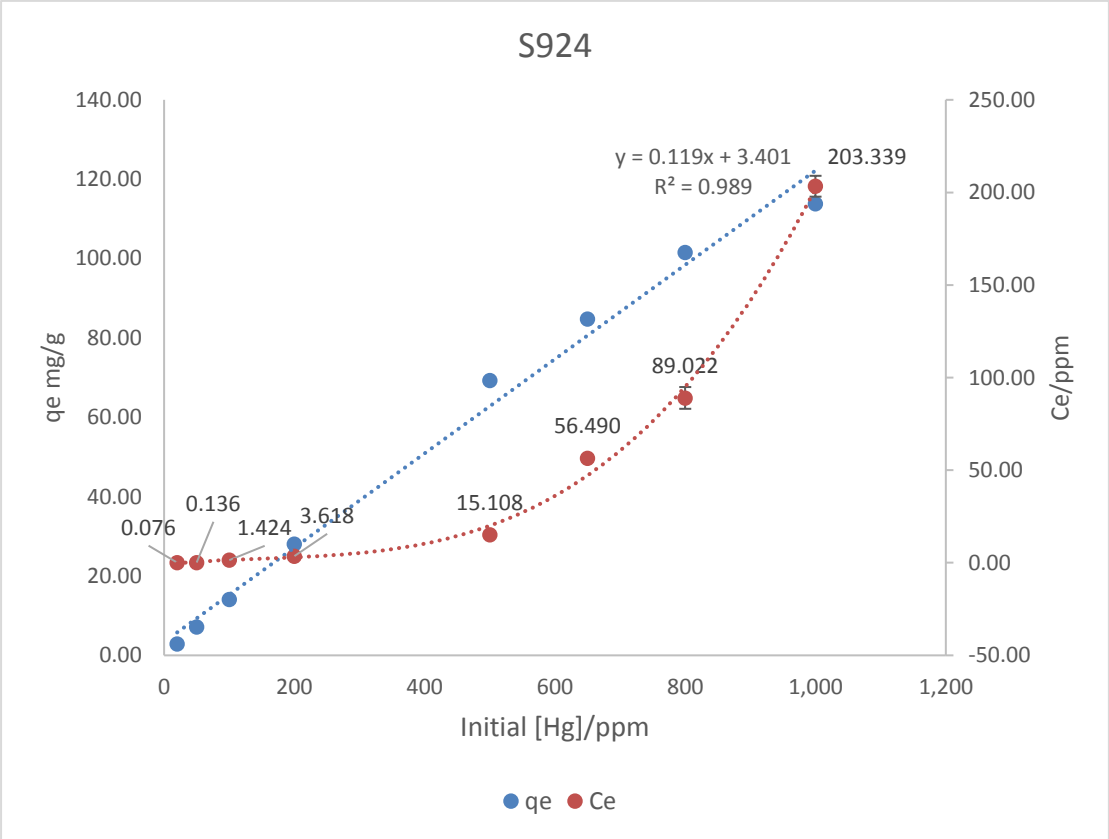


Figure 4- 8 Impact of initial mercury concentration (S924). The dosage of S924 was 0.07 g, 10 ml mercury solution, pH 7, 15 hours, 50 rpm, room temperature. The error is standard deviation from triplicate measurements.

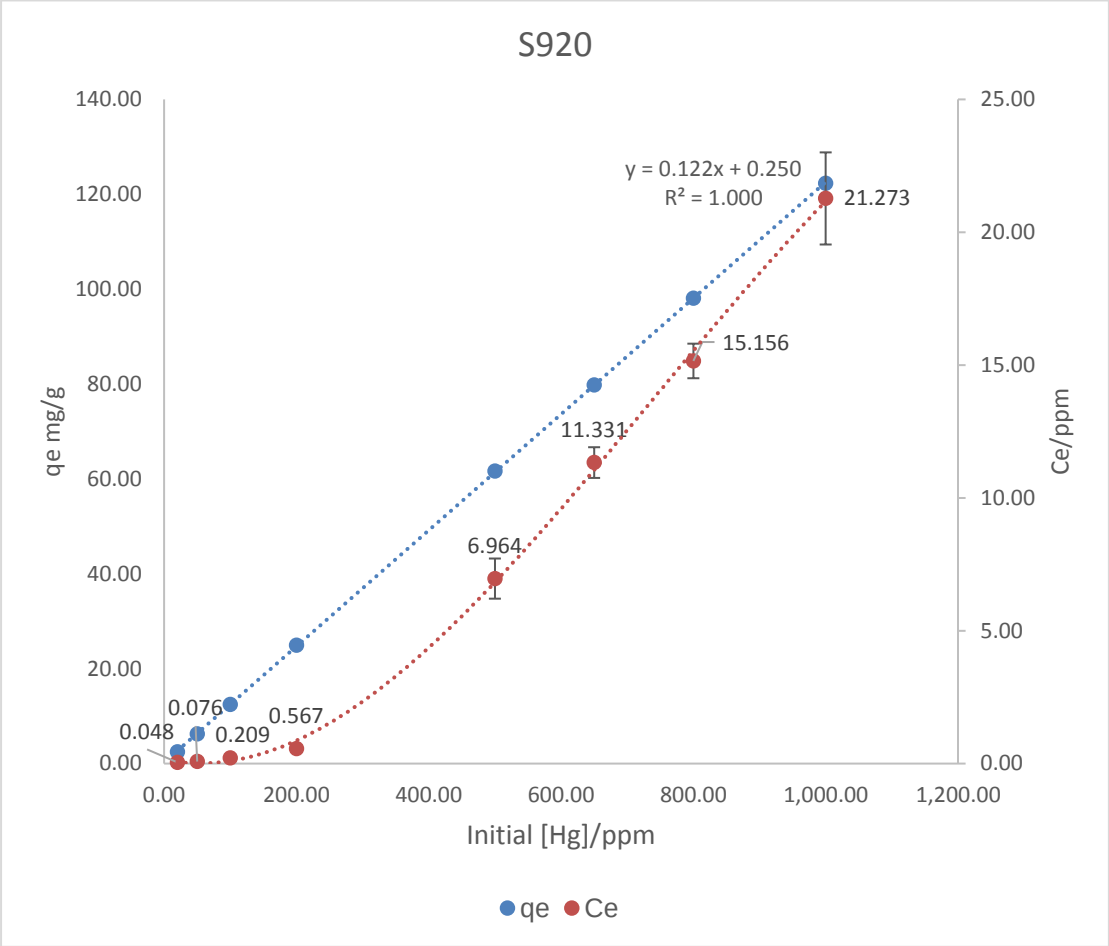


Figure 4-9 Impact of initial mercury concentration (S920). The dosage of S920 is 0.08 g, 10 ml mercury solution, pH 7, 15 hours, 50 rpm, room temperature. The error is standard deviation from triplicate measurements.

4.2.2.3 Adsorption isotherm

The equilibrium relationship of ion exchange resin adsorption is usually described through a diagram known as the adsorption isotherm, which is the functional relationship between the amount of adsorption and equilibrium concentration of the solute in solution at a given constant temperature. The adsorption isotherm of mercury onto resin Purolite S920 and S924 are shown in Fig.4-10, the adsorption capacity increased quickly in the beginning, which indicates that higher adsorption is achieved at lower concentrations of Hg. For the resin adsorption, it is the type I

adsorption isotherm according to the classification, here two main favourable models of isotherm are Langmuir and Freundlich theory, the isotherm equations of them are shown below [85]:

Langmuir: $$q_e = \frac{q_{max} b C_e}{1 + b C_e} \quad (8)$$

Freundlich: $$q_e = K_F C_e^{1/n} \quad (9)$$

Where q_e is the amount of mercury adsorbed per unit weight of resin at equilibrium (mg/g), q_{max} is the maximum monolayer adsorption capacity of the resin (mg/g); Ce is the equilibrium concentration of Hg in solution (ppm); b is the Langmuir isotherm constant (1/ppm); K_F is an empirical constant to represent the adsorption capacity ($mg^{1-1/n}L^{1/n}/g$), a higher value of K_F indicates a higher maximum capacity; 1/n is also an empirical constant to indicate the intensity of adsorption.

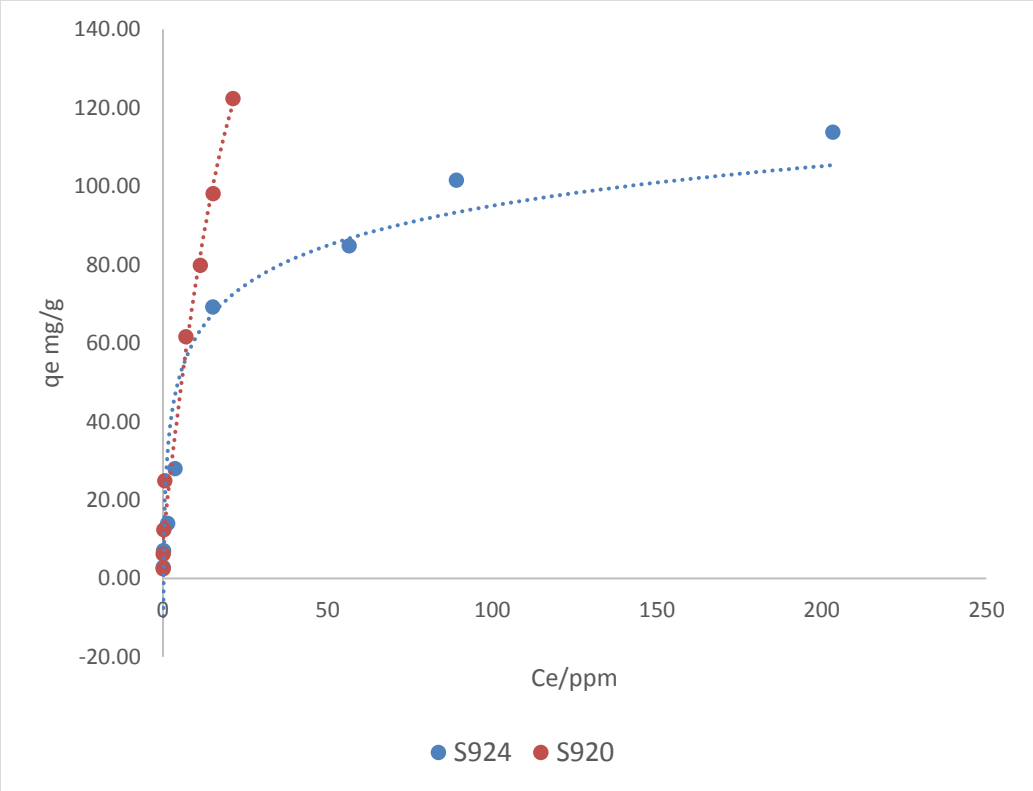


Figure 4-10 Adsorption isotherms of mercury onto Purolite S920 and S924. The error is standard deviation from triplicate measurements.

The Eq. (8) can be rearranged to Eq. (10), the value of q_{max} and b can be evaluated by making a plot of $1/q_e$ versus $1/C_e$.

$$\frac{1}{q_e} = \frac{1}{q_{max} b C_e} + \frac{1}{q_{max}} \quad (10)$$

The Eq. (9) can be wrote as: $\ln q_e = \ln K_F + \frac{1}{n} \ln Ce$ (11), K_F and n can be calculated by plotting $\ln q_e$ versus $\ln C_e$.

Table 4-3 shows the parameters of these two models used for the adsorption onto Purolite S924 and S920, R^2 is the corresponding coefficient. The maximum adsorption capacity of S920 calculated out by Langmuir model is 222.22 mg/g, which is much bigger than the experimental adsorption capacity (123.81 mg/g). For both Purolite S924 and S920, the Freundlich isotherm model fits better for the adsorption of mercury than the Langmuir due to its higher corresponding coefficient.

Lloyd-jones et al. [67] used ion exchange resin Purolite S920 and GT-73 (a different ion exchange resin with thiol groups) to capture $HgCl_2$ from aqueous solution, the sorption isotherm study was similar to that here, in these experiments, and a Freundlich isotherm model for S920 was derived, with K_F value of 4.91 and n of 1.91.

Table 4- 3 Parameters of Langmuir and Freundlich isotherm models

	Langmuir			**Freundlich**		
	q_{max} (mg/g)	**b (1/ppm)**	**R^2**	**K_F ($mg^{1-1/n}L^{1/n}/g$)**	**n**	**R^2**
Purolite S924	112.43	0.72	0.9206	13.48	2.19	0.9664
Purolite S920	222.22	0.27	0.9399	22.90	1.80	0.9617

4.2.2.4 Impact of pH

For resin Purolite S924, Fig. 4-11 shows the pH dependency of mercury uptake efficiency from solution. The extraction efficiency is strongly dependent on the initial

pH of the solutions with enhancement of extraction as the pH was increased from 5 to 8. When the solution is under an alkaline condition, the adsorption efficiency can be over 90%, higher than the efficiency at acid condition. It may due to the competition between H^+ and Hg^{2+}, hydrogen ion may prevent the formation of Hg-thiol complexes when the initial solution is acid. Furthermore, pH decreased with time during the adsorption of mercury by ion exchange resin, it dues to the ion exchange mechanism, H^+ was released to solution when Hg^{2+} was bonded with S atoms of thiol-modified resin. The final pH value was reduced to around 2 when initial pH was 9-10, and to about 4 when the initial pH was 4-6.

The final pH value depends on the initial Hg concentration in solution and the Hg removal efficiency. The greater the initial Hg concentration and removal efficiency, the lower the final pH obtained. For example, with a solution with initial Hg^{2+} concentration of 0.05 mol/L, after theoretical 100% removal of mercury by a thiol ion exchange resin, according to the balance of positive charges the final concentration of H^+ in solutions can be calculated to 0.1 mol/L, the pH is equal to 1.

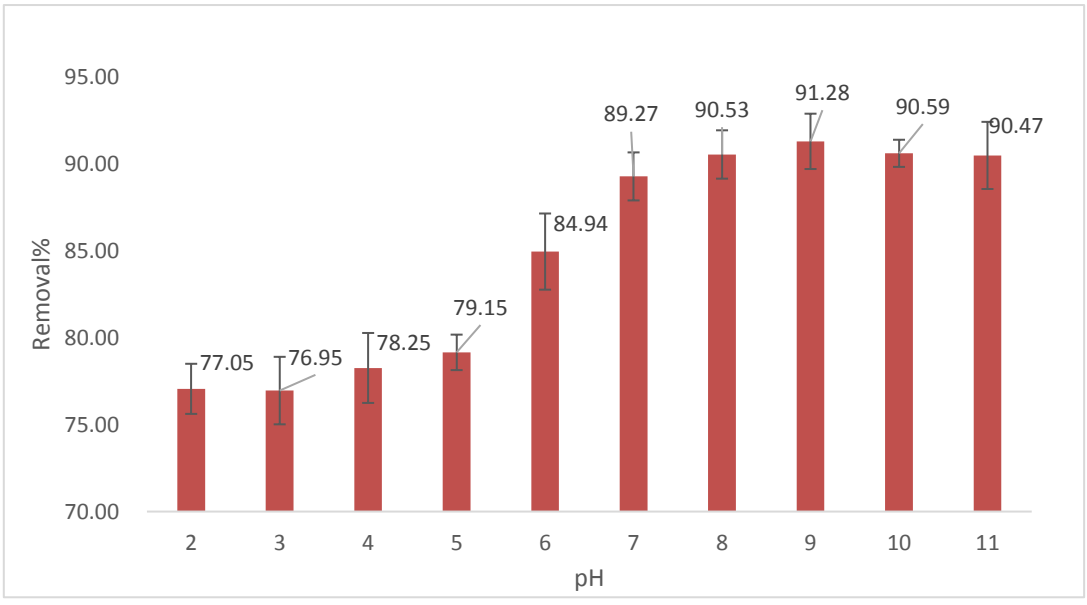


Figure 4-11 Impact of solution pH on mercury removal by using S924. The dosage of S924 was 0.07 g, 10 ml 1000 ppm mercury solution, room temperature, 15 h, 50 rpm stirring.

With Purolite S920, the result of the influence of pH on mercury capture from solutions was contrary to S924, Fig.4-12 indicated the adsorption of mercury performed worse by using S920 under alkaline conditions. The removal efficiency was higher over a pH range of 5 to 8, and was optimal at pH 7. Purolite S920 is thiouronium resins, which can be readily hydrolysed under alkaline condition, the chemical character changes when the thiouronium functional group is lost from these resins. If the below reaction took place, mercury may leak out by forming complexes with urea via oxygen electron donor atom [72], then the amount of mercury adsorbed by thiouronium resin decreased.

$$[\mathrm{R\text{-}CH_2\text{-}S\text{-}C(NH_2)_2}]^{+}X^{-} + \mathrm{NaOH} \rightarrow \mathrm{R-CH_2\text{-}SH} + \mathrm{OC(NH_2)_2} + \mathrm{NaX} \quad [86]$$

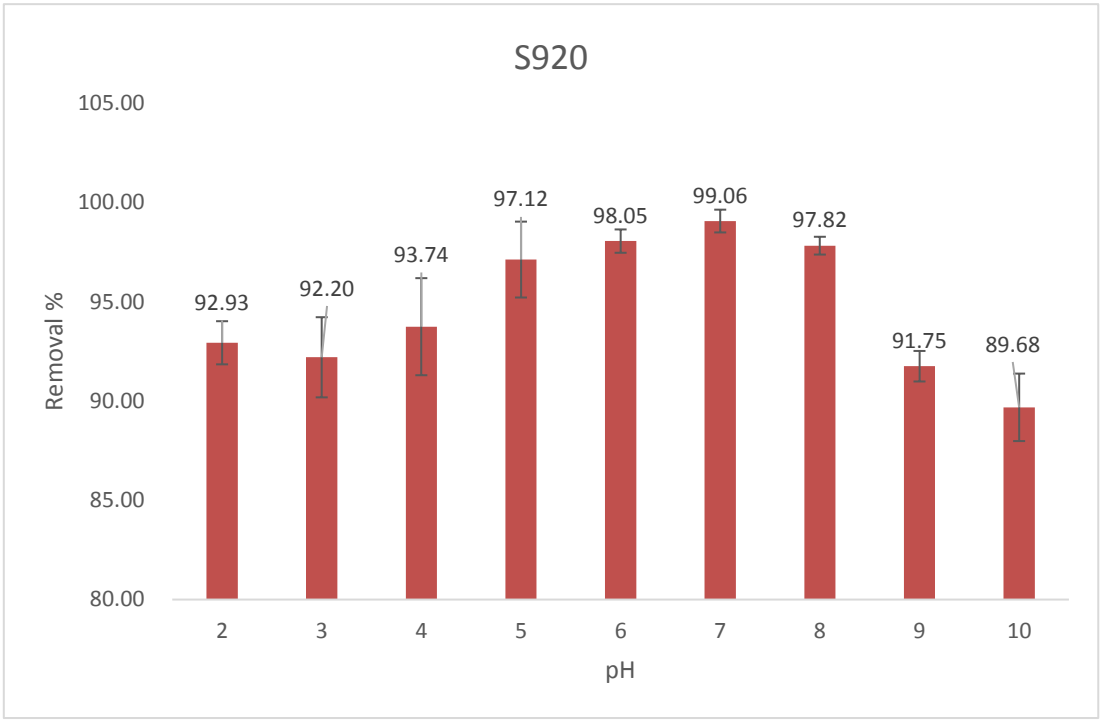


Figure 4-12 Impact of solution pH on mercury capture by using S920. The dosage of s920 was 0.08 g. 10 ml 1000 ppm mercury solution, room temperature, 15 h, 50 rpm stirring. The error is standard deviation from triplicate measurements.

4.2.2.4 Impact of temperature

Figure 4-13 and Figure 4-14 show the influence of temperature on adsorption of Purolite S924 and S920. Obviously, the rate of adsorption increased with an increase of temperature, thus the equilibrium time is shorter at higher temperature. After a full contact of solution and adsorbent, the adsorption achieved an equilibrium state and the removal efficiency or adsorption capacity had a maximum value for each temperature. For both resin S924 and S920, the higher the temperature is, the quicker the extraction of Hg is. In these stirred vial tests, Purolite S924 took approximately 420 min (or 7 h) to reach extraction equilibration with the aqueous mercury containing feed (with a final removal efficiency of 91.17±1.03%) at room temperature. At 35 ºC, equilibration was achieved in 300 min (5 h) and at 45 ºC this was further reduced to 180 min (3 h) as shown in Fig. 4-13. For Purolite S920, in equivalent experiments, it took approximately 300 min, 180 min and 120 min to achieve a 99% mercury removal efficiency at 25 ºC, 35 ºC and 45 ºC respectively (Fig. 4-14). The colour of Hg-containing (iodomercurate) solution was observed to change from yellow to colourless transparent, which means most soluble mercury had been absorbed by those ion exchange resin after a sufficient contact.

Temperature is an indicator to judge an adsorption reaction is an exothermic or endothermic process, here the adsorption onto Purolite S924 and S920 are endothermic because the adsorption ability increased with the increasing of temperature. The phenomenon means the interaction between resin and mercury solution needs energy to support it. Besides, the increasing temperature can enhance the molecules' mobility of mercury solution and increase the number of active sites of resin, that's why mercury can be adsorbed more quickly at higher temperature.

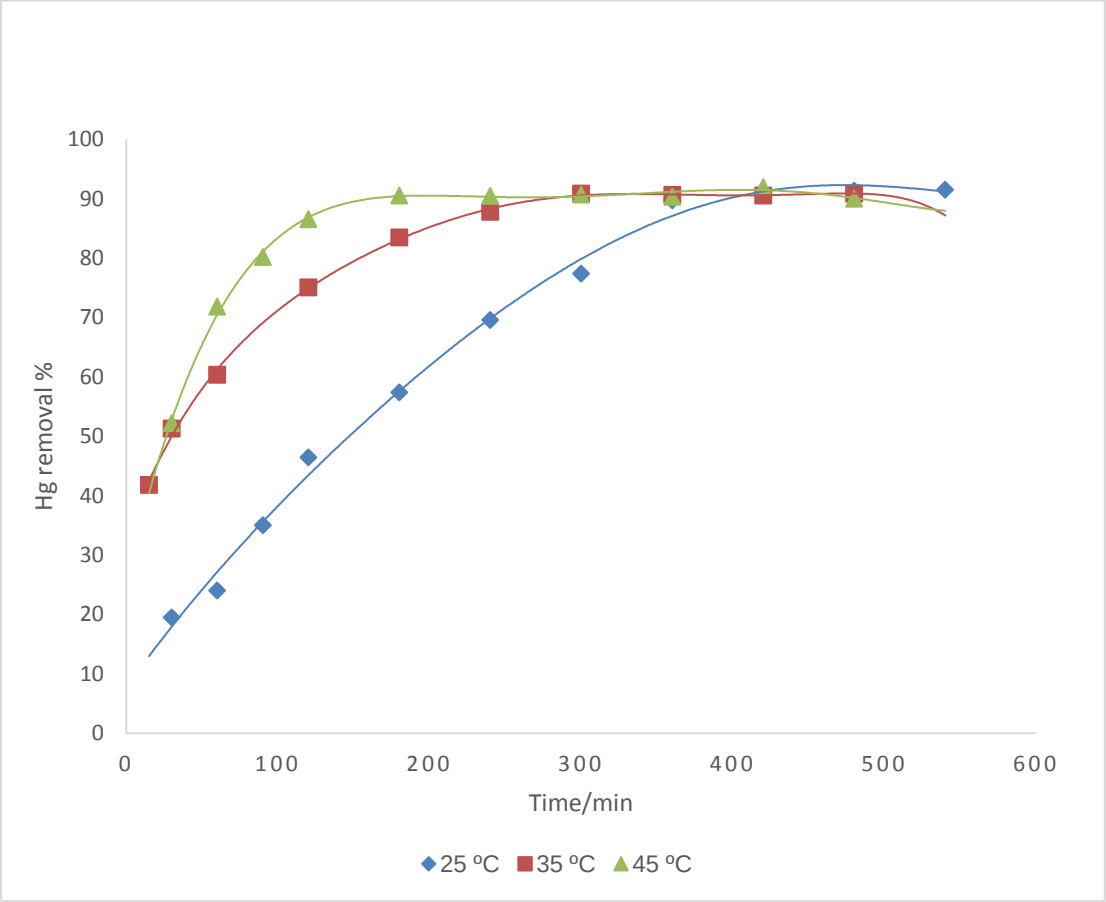


Figure 4- 13 Impact of temperature on mercury capture by using S924. The dosage of S924 is 0.07 g, volume and initial mercury concentration of solution were 10 ml and 1000 ppm respectively, initial pH was 9, stir at 50 rpm.

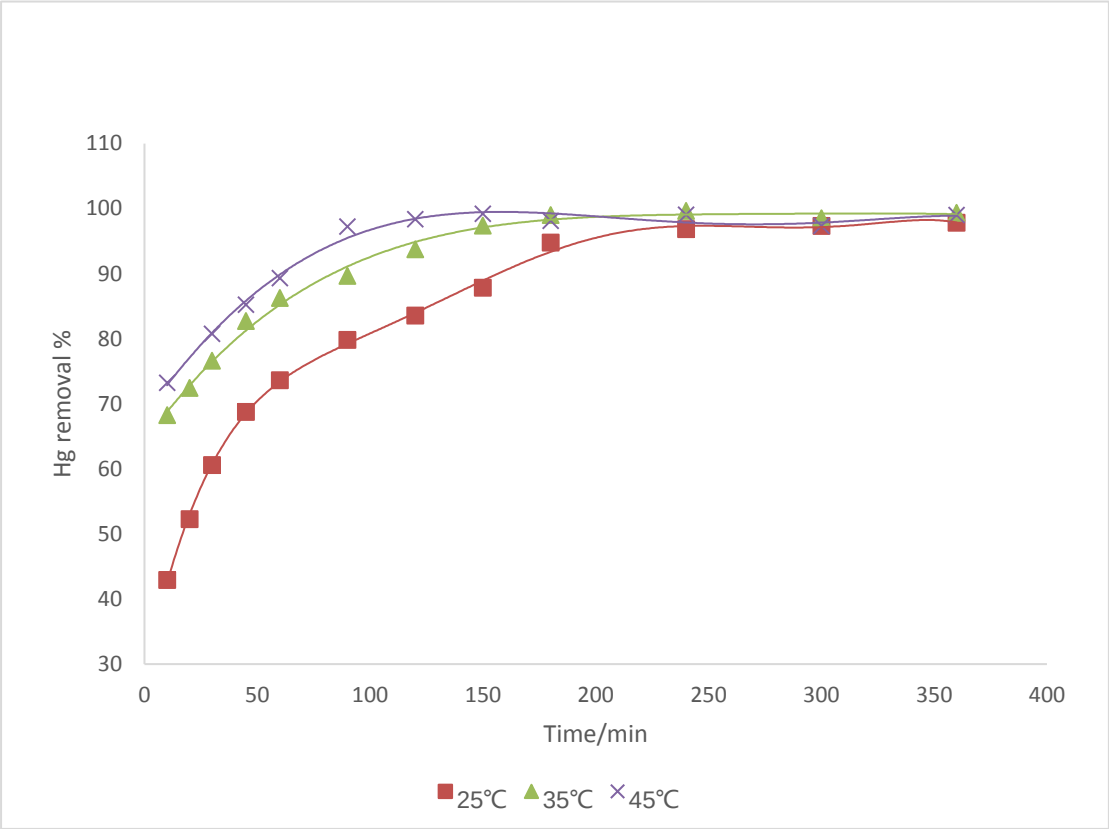


Figure 4- 14 Impact of temperature on mercury capture by using S920. The dosage of S920 is 0.08 g, volume and initial mercury concentration of solution were 10 ml and 1000 ppm respectively, initial pH was 8, stir at 50 rpm.

4.2.2.5 Kinetics study

The adsorption kinetics of Purolite S924 and S920 can be studied through Fig.4-13 and Fig.4-14, the kinetics of mercury recovery increased when temperature increased from 25 ºC to 45 ºC. Fig.4-15 illustrated the adsorption kinetics (q_t vs t, [66, 87]) onto S924 and S920 at initial Hg concentration of 1000 ppm and room temperature, the adsorption capacity increases with time until equilibrium is achieved. At first (within 100 min), the adsorbed amount of mercury increased quickly with time, and then the slope of q_t versus time decreases with time until it becomes flat at equilibrium. The maximum adsorption capacity for S924 and S920 achieved were 129.36±1.94 and 123.98±3.23 mg/g, respectively. As mentioned in table 1.6, the maximum reported

mercury capacity by Purolite for S924 and S920 can be calculated based on the capacity of 200 g/L and resin gravity of 1.1 g/ml, which is 181.81 mg/g. The maximum adsorption capacity of mercury achieved by experiment was lower than the reported value, it means the initial concentration range of Hg and resin dosage (eq. 7) is not optimal for the treatment of mercury in solutions, there has surplus capacity for S924 and S920 to adsorb mercury in this case.

For ion exchange systems, the process kinetics include: solution film diffusion, diffusion inside the particle and rate of reaction [66, 69]. In many practical cases and previous study, mass transfer occurs through a combination of these mechanisms. The initial rate of adsorption is very fast, and then the rate decreased with time. This may due to the external mass transfer in liquid bulk, mercury ions are bonded with the enough amounts of active sites on the resin's surface in the beginning, the resistance of external mass transfer is not big so that the initial kinetics is rapid. After most active sites or atoms in the surface of resin have been occupied by mercury ions, the rate-control step transforms the path from external to intra-particle diffusion, therefore, the rate of adsorption of mercury decreased, and the transport phenomena inside particles can be regarded as the limiting-step. These facts can be described by using mathematical models such as pseudo first order and pseudo second order.

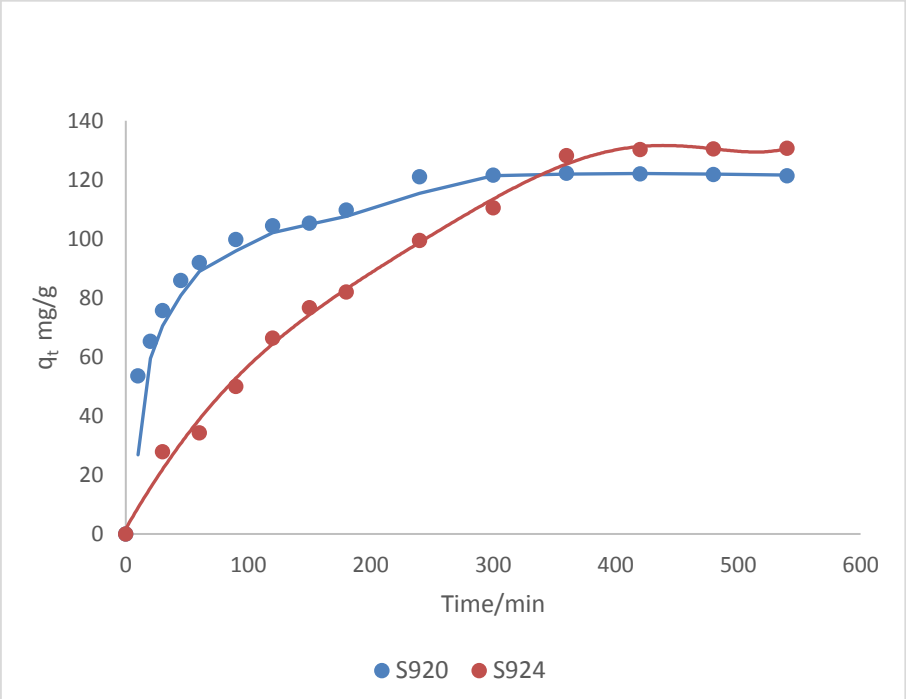


Figure 4- 15 Adsorption kinetics onto Purolite S924 and S920. Initial Hg concentration was 1000 ppm, dosage of S924 and S920 was 0.07 g and 0.08 g respectively, stirred at 50 rpm, room temperature.

Models of pseudo first order and second order are frequently applied to analyse the adsorption of mercury using the equations shown below [87]:

Pseudo first order:

$$q_t = q_e [1 - e^{-k_1 t}] \quad (12)$$

Pseudo second order:

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \text{ or } \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (13)$$

Where qt (mg/g) is the amount of Hg adsorbed at time t (t, min); k_1 (L/min) is the adsorption rate constant of pseudo first order obtained from the linear plot of ln (qe-qt) versus t; k_2 (g/mg·min) is the rate constant of pseudo second order obtained from the plot of t/qt versus t.

Table 4-4 indicates the result of how adsorption kinetics fit these two models. Compared to pseudo first order, pseudo second order showed a better linear relationship, the value of R^2 was close to 1. What's more, the value of maximum adsorption capacity calculated from pseudo second order was closer to the experimental value. Therefore, the mercury adsorption results of Purolite S924 and S920 followed pseudo second order kinetics. Generally, the pseudo-first-order kinetic equation is suitable for the initial stage of the adsorption process, while the pseudo-second-order can more comprehensively reflect a series of chemical processes such as liquid film diffusion, intraparticle diffusion during the adsorption of Hg^{2+} by Purolite S924 and S920 resin [66, 88].

Table 4- 4 Parameters of the kinetic models of Purolite S924 and S920.

			Pseudo first order			**Pseudo second order**		
	Con. ppm	Temperature	q_e(mg/g)	k_1 (L/min)	R^2	q_e(mg/g)	k_2 (g/mg/min) x10^3	R^2
S924	1000	25ºC	333.82	0.0137	0.8969	147.06	0.1163	0.9810
		35ºC	111.25	0.0151	0.9697	140.85	0.1723	0.9979
		45ºC	166.80	0.0296	0.9929	144.93	0.2814	0.9981
S920	1000	25ºC	68.68	0.0110	0.9702	125.00	0.4863	0.9997
		35ºC	53.68	0.0208	0.9134	126.58	0.9499	0.9997
		45ºC	41.12	0.0227	0.9507	125.00	1.4512	0.9994

The value of k_1 and k_2 increased with the increasing of temperature, the rising of rate constant is attributed to the increasing mobility of mercury molecules caused by the rise of temperature. It's possible to calculate the activation energy according to the Arrhenius equation [69]:

$$k = Ae^{-E_a/(RT)} \quad (13)$$

Activation energy can be calculated from the value of slope by plotting $\ln k_2$ versus 1/T.

The activation energy was achieved of 4.31±1.08 kJ/mol for S920 and 34.74±2.89 kJ/mol for S924.

4.2.2.6 Summary of mercury extraction by Purolite S924 and S920

Purolite S924 is polystyrene based chelating resin with a functional group of thiol, while Purolite S920 has the functional group of thiouronium. The effectiveness of mercury removal from aqueous solutions by ion exchange resin is strongly dependent on their functional groups. The maximum removal efficiency was achieved of 84.28±0.71% and 99.16±1.91% by 0.07g S924 and 0.08 g S920, respectively. S920 is more effective than S924 due to its functional group has both sulphur and amine groupings. The efficiency of mercury removal is dependent on initial mercury concentration, the adsorption efficiency increased with a decrease of initial Hg concentration, the ion exchange resin is more effective when Hg concentration is below 100 ppm. The Freundlich model displays a better fit for the adsorption on S924 and S920 and maximum adsorption capacities of 129.36±1.94 and 123.98±3.23 mg/g for Purolite S924 and S920 respectively were obtained. It is recommended for S924 to apply under alkaline condition due to the competition of Hg^{2+} and H^{+}. In contrast, S920 is more effective under neutral condition because Purolite S920 is unstable and easy to hydrolyse under alkaline condition. A pseudo-second-order model can best present the adsorption kinetics of these two resins. Temperature has a positive effect on mercury adsorption, the rate of mercury removal is faster at higher temperature, and the activation energy was achieved of 4.31±1.08 kJ/mol for S920 and 34.74±2.89 kJ/mol for S924.

Chapter 5

Conclusion

A process flow diagram combining and comprising the main steps of Hg dissolution and mercury capture from solutions is illustrated in Fig.5-1. Iodine has a good solubility in iodide solution, potassium iodide and iodine solution was studied as a good method to dissolve elemental mercury by forming soluble mercury compounds of $[HgI_4]^{2-}$. It was found that an increase in KI/I_2 solution concentration can improve the solubility of mercury. To achieve a complete dissolution of 100 mg elemental mercury and to obtain less chemical consumption, a solution concentration of 4% (0.053/0.16 M I_2/KI) w/v potassium iodide and iodine and a minimum contact time for mercury dissolution of 10 hours are suggested, the mercury concentration dissolved in KI/I_2 solution was 0.050±0.002 mol/L, which represents 100.7±3.8% solubility efficiency. The effectiveness of mercury dissolution in KI/I_2 solution was examined dependent on solution concentration, solution pH, molar ratio of I_2: KI and temperature. Therefore, in this experiment, potassium iodide is recommended a little excess in case the formation of insoluble HgI_2, a 10 ml potassium iodide/iodine (3:1) solution with a concentration of 4% (0.053/0.16 M I_2/KI) w/v under mild or neutral condition was recommended to apply to dissolve 100 mg (0.5 mmol) elemental mercury at room temperature with a 50-rpm stirring speed. Temperature can increase the dissolving rate of mercury and thus reduce the contact time, however, temperature above 65 °C is not suggested because it costs too much energy and leads to a loss of iodine.

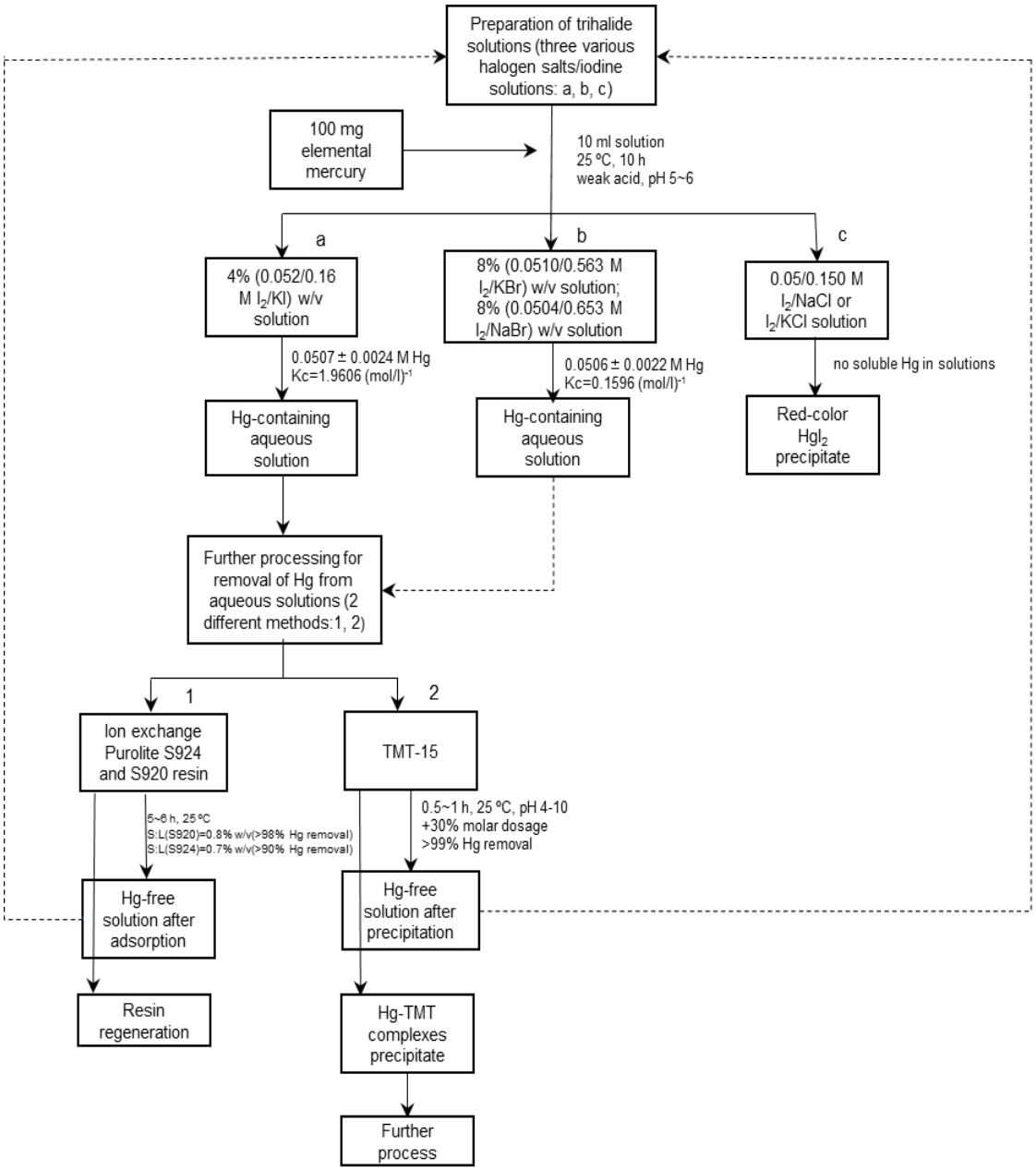


Figure 5- 1 A process flow diagram combining and comprising the main steps of elemental mercury dissolution and mercury capture from solutions.

Bromide/iodine solutions were studied as potentially useful alternatives to the KI/I_2 system to dissolve elemental mercury, but were found to be less effective than iodide/iodine solution. It was more difficult to dissolve iodine in the bromide solutions, requiring a greater bromide salt concentration to enable solubilisation. The equilibrium

constant Kc of mercury dissolution in halogen sodium bromide/iodine and potassium iodine solution was 0.16 and 0.12 $(mol/l)^{-1}$ respectively, which is smaller than it of potassium iodide/iodine solution (1.96 $(mol/l)^{-1}$). To completely dissolve 100 mg mercury, the optimal KBr/I_2 solution was suggested to use 8% (0.051/0.563 M I_2/KBr), the mercury concentration after leaching was achieved of 0.051±0.001 mol/L, with a solubility efficiency of 101.4±4.4%. The optimal $NaBr/I_2$ solution was 8% (0.0504/0.6531 M I_2/NaBr) and it leaded to a mercury concentration of 0.0506±0.0009 mol/L, which indicates about 101.2±4.1% of mercury was dissolved in solutions. To achieve a same mercury concentration in solution, more mass or molar amount of bromide salts are needed than iodide.

Chloride salt/iodine solution performed poorly on mercury dissolution because iodine was found to be very poorly soluble in the chloride solutions and reaction with elemental mercury resulted in formation of insoluble HgI_2 precipitate rather than soluble halomercurate(II) anions. Chloride/iodine is not an effective and economic way to dissolve mercury in solutions.

The use of Purolite S924/ S920 ion exchange resins as extractants and TMT-15 as a precipitant to remove the solubilised mercury(II) ions from aqueous solution was investigated. The residual mercury concentration after precipitation of 0.028±0.025 g/L was achieved by using 30% molar excess dosage (0.7 g) of TMT-15 The advantage of TMT-15 to remove mercury is: (a) it is effective over a wide operating pH range, with an efficiency was above 90% over a solution pH range from 4 to 10, TMT-15 is suggested to applied under alkaline condition due to the higher efficiency; (b) Mercury-TMT complexes are chemically and thermally stable and have no decomposition over time; (c) It doesn't produce toxic by-products, it's safe to operate; (d) The contact time for TMT-15 to precipitate with mercury is very quick, it only took about 1 hour to remove almost 10000 ppm (10 ml) mercury from aqueous solutions. TMT-15 is efficient to treat Hg-containing wastewater with high concentration (>100

ppm) of dissolved mercury.

Ion exchange resins containing thiol and thiouronium groups, designed for mercury removal in waste water treatment were also investigated. It was found that these are most effective for treating solutions with low concentrations of mercury (<100 ppm) and that the removal efficiency was highest at low mercury concentration. The final concentration of mercury obtained with S920 and S924 resins was 0.048±0.015 and 0.076±0.006 ppm respectively when the initial concentration of mercury was 20 ppm. Adsorption of mercury onto Purolite resin could be applied as a secondary treatment of mercury extraction following the chemical precipitation of TMT-15 to achieve a lower Hg concentration and to meet mercury discharge limits.

The effectiveness of mercury removal from aqueous solutions by ion exchange resin is strongly dependent on their functional groups. Purolite S920 was more effective than S924 due to the presence of both sulphur and amine groups of S920. The maximum removal efficiency achieved after 5-6 h contacting was 84.28±0.71% and 99.16±1.91% using S924 (0.07 g) and S920 (0.08 g), respectively. The efficiency of mercury removal is dependent on initial mercury concentration, solution pH, contact time and temperature. S924 is suggested to apply under alkaline condition due to the competition of Hg^{2+} and H^{+}. S920 is more effective under neutral or mild condition because Purolite S920 is unstable to hydrolysis under alkaline condition. The Freundlich model is better fit for the adsorption on S924 and S920, the maximum adsorption capacity was 129.36±1.94 and 123.98±3.23 mg/g for Purolite S924 and S920 respectively. The pseudo-second-order can best represent the adsorption kinetics of these two resins. Temperature has a positive effect on mercury adsorption, the rate of mercury removal is faster at higher temperature, and the activation energy was calculated of 4.31±1.08 kJ/mol for S920 and 34.74±2.89 kJ/mol for S924.

For the future work, it will study whether the concentration of iodide have an influence

on the efficiency of capture soluble mercury from aqueous solutions by using Resin S924 and S920. What's more, analyse the in situ mercury remediation from oil pipelines to see whether these methods in this project is effective to remove mercury or to see what's the difference of results between the lab-scale and full-scale.

References

1. *Mercury management in petroleum refining.* IPIECA, 2014: p. 36.

2. Gaffney, J. and N. Marley, *In-depth review of atmospheric mercury: sources, transformations, and potential sinks.* Energy and Emission Control Technologies, 2014: p. 1.

3. Antoszczyszyn, T. and A. Michalska, *The potential risk of environmental contamination by mercury contained in Polish coal mining waste.* Journal of Sustainable Mining, 2016. **15**(4): p. 191-196.

4. Reichelt-Brushett, A.J., et al., *Geochemistry and mercury contamination in receiving environments of artisanal mining wastes and identified concerns for food safety.* Environmental Research, 2017. **152**: p. 407-418.

5. Tunsu, C., et al., *Investigations regarding the wet decontamination of fluorescent lamp waste using iodine in potassium iodide solutions.* Waste Management, 2015. **36**: p. 289-296.

6. Wilhelm, S.M. and N. Bloom, *Mercury in petroleum.* Fuel Processing Technology, 2000. **63**(1): p. 1-27.

7. Sanchez, G.S., *Mercury in extraction and refining process of crude oil and natural gas.* 2013: p. 68.

8. Keller, S.G. and A.P. Gordon, *Experimental study of liquid metal embrittlement for the aluminum 7075–mercury couple.* Engineering Fracture Mechanics, 2012. **84**: p. 146-160.

9. Gonzalez-Raymat, H., et al., *Elemental mercury: Its unique properties affect its behavior and fate in the environment.* Environmental Pollution, 2017. **229**: p. 69-86.

10. *Water vapor pressure*. 2017 [cited 2017 29/9]; Available from: http://webbook.nist.gov/cgi/cbook.cgi?ID=C7732185&Mask=4.

11. Katrinak, K.A., et al., *Mercury in North Dakota lignite.* Fuel Processing Technology, 1994. **39**(1): p. 35-45.

12. Fisher, J.F., *Elemental mercury and inorganic mercury compounds; human health aspects.* World Health Organization, 2003(1020-6167): p. 2-17.

13. *Mercury(II) oxide*. 2016 [cited 2016 03/11]; Available from: https://en.wikipedia.org/wiki/Mercury(II)_oxide.

14. Wikimedia. *Mercury(II) iodide*. 2017 [cited 2017 30/11]; Available from: https://en.wikipedia.org/wiki/Mercury(II)_iodide.

15. Mahaffey, K.R., *Mercury exposure: medical and public health issues.* Trans Am Clin Climatol Assoc, 2005. **116**: p. 127-53; discussion 153-4.

16. Wang, J., et al., *Remediation of mercury contaminated sites – A review.* Journal of Hazardous Materials, 2012. **221**: p. 1-18.

17. *Guidance on the Identification, Management and Remediation of Mercury Contaminated Sites* IPEN, 2016: p. 10-22.

18. *Global Atmospheric Mercury Assessment: Sources, Emissions and Transport.* United Nations Environment Programme (UNEP), 2015: p. 12-34.

19. Qian, J., et al., *Distribution of Mercury Pollution and Its Source in the Soils and Vegetables in Guilin Area, China.* Bulletin of Environmental Contamination and Toxicology, 2009. **83**(6): p. 920.

20. *Evaluation of certain food additices and contaminants.* WHO Technical Report Series, 2004(0512-3054).

21. E.A. Bailey, J.E.G., and P.M. Theodorakos *Mercury in vegetation and soils at abandoned mercury mines in southwestern Alaska, USA.* Science for a changing world, 2002. **2**(3): p. 275-285.

22. Feng, X., et al., *Gold mining related mercury contamination in Tongguan, Shaanxi Province, PR China.* Applied Geochemistry, 2006. **21**(11): p. 1955-1968.

23. Pataranawat, P., et al., *Mercury emission and distribution: Potential environmental risks at a small-scale gold mining operation, Phichit Province, Thailand.* J Environ Sci Health A Tox Hazard Subst Environ Eng, 2007. **42**(8): p. 1081-93.

24. Bernaus, A., et al., *Determination of mercury in polluted soils surrounding a chlor-alkali plant.* Analytica Chimica Acta, 2006. **565**(1): p. 73-80.

25. Grangeon, S., et al., *Lichen and soil as indicators of an atmospheric mercury contamination in the vicinity of a chlor-alkali plant (Grenoble, France).* Ecological Indicators, 2012. **13**(1): p. 178-183.

26. Xu, J., et al., *Sources and remediation techniques for mercury contaminated soil.* Environment International, 2015. **74**: p. 42-53.

27. Celia D.A. Earle, R.D.R., Jonathan F. K. Earle, *Mercury in a municipal solid waste landfill.* Waste Management & Research 1999. **17**: p. 305-312.

28. Chai, X., et al., *The dependence of the methylation of mercury on the landfill stabilization process and implications for the landfill management.* Chemosphere, 2015. **119**: p. 828-834.

29. Morel, F.M.M., A.M.L. Kraepiel, and M. Amyot, *The chemical cycle and bioaccumulation of mercury.* Annual Review of Ecology and Systematics, 1998. **29**(1): p. 543-566.

30. Mason, R.P., W.F. Fitzgerald, and F.M.M. Morel, *The biogeochemical cycling of elemental mercury: Anthropogenic influences.* Geochimica et Cosmochimica Acta, 1994. **58**(15): p. 3191-3198.

31. Mason, R.P., *Mercury emissions from natural processes and their importance in the global mercury cycle. In N. Pirrone & R. Mason (Eds.).* Mercury Fate and Transports in the Global Atmosphere Springer, 2009: p. 173-199.

32. Wilson, S., Kindbom, K., Yaramenka, K., Steenhuisen, F, *Part A: global emissions of mercury to the atmosphere.* UNEP/AMAP 2012, Techincal Report, 2012. **2017**(10/8).

33. Wang, S. and K. Luo, *Atmospheric emission of mercury due to combustion of steam coal and domestic coal in China.* Atmospheric Environment, 2017. **162**: p. 45-54.

34. Interior, U.S.D.o., *Mercury contamination of aquatic ecosystems.* Science for a changing world, 1995(FS-216-95): p. 1-4.

35. Pirrone, N., et al., *Global mercury emissions to the atmosphere from anthropogenic and natural sources.* Atmos. Chem. Phys., 2010. **10**(13): p. 5951-5964.

36. *Liquid metal embrittlement by mercury in the refining and allied process industries*. 2014 [cited 2017 6/3]; Available from: http://www.hse.gov.uk/safetybulletins/lme-by-mercury.htm.

37. *Treatment technologies for mercury in soil, waste, and water.* U.S Environmental Protection Agency, 2007: p. 1-133.

38. Anacleto, A.L. and J.R. Carvalho, *Mercury cementation from chloride solutions using iron, zinc and aluminium.* Minerals Engineering, 1996. **9**(4): p. 385-397.

39. Zhang, J. and P.L. Bishop, *Stabilization/solidification (S/S) of mercury-containing wastes using reactivated carbon and Portland cement.* Journal of Hazardous Materials, 2002. **92**(2): p. 199-212.

40. B.Bowerman, J.A., P.Kalb, R-Y. Wan, M.LeVier, *Using the Sulfur Polymer Stabilization/Solidification Process to Treat Residual Mercury Wastes from Gold Mining Operations. February.* Society of Mining Engineers Conference, 2003(BNL-71499-2003-CP): p. 1-10.

41. Hulet, G.A.M., Vincent Carl Morris, M.I, *Demonstrations to Support Change to the >260 ppm Mercury Treatment Regulations* University of North Texas Libraries, Digital Library, 2001: p. 1-10.

42. Visvanathan, C., *Treatment and Disposal of Mercury Contaminated Waste from Oil and Gas Exploration Facilities*. 2017.

43. Chang, T.C. and J.H. Yen, *On-site mercury-contaminated soils remediation by using thermal desorption technology.* Journal of Hazardous Materials, 2006. **128**(2): p. 208-217.

44. Massacci, P., L. Piga, and M. Ferrini, *Applications of physical and thermal treatment for the removal of mercury from contaminated materials.* Minerals Engineering, 2000. **13**(8): p. 963-967.

45. Busto, Y., et al., *Potential of thermal treatment for decontamination of mercury containing wastes from chlor-alkali industry.* Journal of Hazardous Materials, 2011. **186**(1): p. 114-118.

46. Rumayor, M., et al., *An assessment of the environmental fate of mercury species in highly polluted brownfields by means of thermal desorption.* Journal of Hazardous Materials, 2017. **325**: p. 1-7.

47. Huang, Y.-T., Z.-Y. Hseu, and H.-C. Hsi, *Influences of thermal decontamination on mercury removal, soil properties, and repartitioning of coexisting heavy metals.* Chemosphere, 2011. **84**(9): p. 1244-1249.

48. Kucharski, R., et al., *A Method of Mercury Removal from Topsoil Using Low-Thermal Application.* Environmental Monitoring and Assessment, 2005. **104**(1): p. 341-351.

49. Narongsak Chaiyasit, C.K., Sheila Yeh, Darrell Gallup, Lyman Young, *Decontamination of mercury contaminated steel of API 5L-X52 using iodine and iodide lexiviant.* Modern Applied Science, 2010. **4**(1913-1852): p. 1.

50. Zhou, Z. and D. Dreisinger, *An investigation of mercury stabilization techniques through hypochlorite leaching and thiosulfate/selenosulfate precipitation.* Hydrometallurgy, 2017. **169**: p. 468-477.

51. Isaia, F., et al., *Gold and palladium oxidation/complexation in water by a thioamide-iodine*

leaching system. Green Chemistry, 2017.

52. Barbara A. Weir, N.K.C., John E. Litz, Donald W. Whisenhunt, , *Mercury removal from doe solid mixed waste using the GEMEP technology.* IAEA INIS, 1999. **33**(02).

53. Cai, J., et al., *Removal of elemental mercury by clays impregnated with KI and KBr.* Chemical Engineering Journal, 2014. **241**: p. 19-27.

54. Blue, L.Y., P. Jana, and D.A. Atwood, *Aqueous mercury precipitation with the synthetic dithiolate, BDTH2.* Fuel, 2010. **89**(6): p. 1326-1330.

55. Patterson, J.W., *Industrial wastewater treatment technology, Second edition*. 1985: Butterworth Publishers,Stoneham, MA; None. Medium: X; Size: Pages: 512.

56. Matlock, M.M., K.R. Henke, and D.A. Atwood, *Effectiveness of commercial reagents for heavy metal removal from water with new insights for future chelate designs.* Journal of Hazardous Materials, 2002. **92**(2): p. 129-142.

57. *TMT 15® Environmentally friendly separation of heavy metals from wastewater*. [cited 2017 4/5]; Available from: http://www.tmt15.com/product/tmt15/Documents/TMT-15-EN.

58. Henke, K.R., et al., *Chemistry and stability of precipitates from aqueous solutions of 2,4,6-trimercaptotriazine, trisodium salt, nonahydrate (TMT-55) and mercury (II) chloride.* Water Research, 2000. **34**(11): p. 3005-3013.

59. Weiyang, L., Shenyu L.and xueting W., *Treatment of gas field wastewater with high mercury concentration using heavy metal chelator TMT-15.* Environment Protection of Chemical Industry, 2015. **35**(5): p. 461-462.

60. Osantowski, R., *Aqueous Mercury Treatment.* United States Environmental Protection Agency, 1997(625/R-97/004).

61. Matlock, M.M., et al., *Advanced Mercury Removal from Gold Leachate Solutions Prior to Gold and Silver Extraction: A Field Study from an Active Gold Mine in Peru.* Environmental Science & Technology, 2002. **36**(7): p. 1636-1639.

62. Ehadian, M.A., *Mercury contaminated material decontamiantion methods: investigation*. 2001, Hemispheric Center for Environmental Technology: Florida International University. p. 1-73.

63. Lu, X., X. Huangfu, and J. Ma, *Removal of trace mercury(II) from aqueous solution by in situ formed Mn–Fe (hydr)oxides.* Journal of Hazardous Materials, 2014. **280**: p. 71-78.

64. Monteagudo, J.M. and M.J. Ortiz, *Removal of inorganic mercury from mine waste water by ion exchange.* Journal of Chemical Technology & Biotechnology, 2000. **75**(9): p. 767-772.

65. Yavuz, E., B.F. Senkal, and N. Bicak, *Poly(acrylamide) grafts on spherical polyvinyl pyridine resin for removal of mercury from aqueous solutions.* Reactive and Functional Polymers, 2005. **65**(1): p. 121-125.

66. Chiarle, S., M. Ratto, and M. Rovatti, *Mercury removal from water by ion exchange resins adsorption.* Water Research, 2000. **34**(11): p. 2971-2978.

67. Lloyd-Jones, P.J., J.R. Rangel-Mendez, and M. Streat, *Mercury Sorption from Aqueous Solution by Chelating Ion Exchange Resins, Activated Carbon and a Biosorbent.* Process Safety and Environmental Protection, 2004. **82**(4): p. 301-311.

68. *Chelating resin for mercury removal, regenerable*. [cited 2017 10/8]; Available from: http://www.lenntech.com/Data-sheets/Purolite-S924-L.pdf.

69. Ferreira, L.M. and J.M.R. De Carvalho, *Mercury Removal from Chloro-Alkali Plant Waste Waters by Ion Exchange.* Environmental Technology, 1997. **18**(4): p. 433-439.

70. Kagaya, S., M. Gemmei-Ide, and Y. Inoue, *Chelating Resins*, in *Encyclopedia of Polymeric Nanomaterials*, S. Kobayashi and K. Müllen, Editors. 2021, Springer Berlin Heidelberg: Berlin, Heidelberg. p. 1-10.

71. *Technical Data Product Descripition*. [cited 2017 10/8]; Macroporous Thiouronium Chelating Resin]. Available from: http://www.reskem.com/wp-uploads/2015/04/purolite-s920.pdf.

72. Zaganiaris, E., *Ion exchange resins and adsorbents in chemical process.* BOOKS ON DEMAND, 2013. **2**(-10: 2322112917): p. 53-56.

73. *Production Information: Purolite Product Guide.* Purolite, 2015: p. 14-15.

74. Fenili, A. *DMA-80 | the most successful Hg analyzer - Milestone Srl*. 2017 [cited 2017 17/4]; Available from: https://www.milestonesrl.com/en/mercury/dma-80/features.html

75. Yeon, J.-W. and S.-H. Jung, *Effects of temperature and solution composition on evaporation of iodine as a part of estimating volatility of iodine under gamma irradiation.* Nuclear Engineering and Technology, 2017.

76. Denzinger, W.a.H., H. *Patent US4402937 - Preparation of PVP-iodine.* 1983; Available from: https://www.google.com/patents/US4402937.

77. Harman, C.L., *The solubility of iodine in aqueous salt solution*, in *Georgia School of Technology*. 1932.

78. *Potassium bromide*. [cited 2017 11/8]; Available from: http://www.sigmaaldrich.com/catalog/product/sial/p0838?lang=en&region=GB.

79. *Sodium bromide*. [cited 2017 11/8]; Available from: http://www.sigmaaldrich.com/catalog/product/sial/s4547?lang=en&region=GB.

80. Tmt15.com. *MT 15® for heavy metal precipitation*. 2017 [cited 2017 11/8]; Available from: http://www.tmt15.com/product/tmt15/en/about/properties/pages/default.aspx.

81. Fulbright, H.H., M. Leaphart, and V. Van Brunt, *Extraction and Precipitation Chemistry for Mercury Recovery from Aqueous Wastes.* Separation Science and Technology, 1997. **32**(1-4): p. 373-386.

82. Amir Shafeeq, A.M., Waqas Sarfraz, *Mercury removal techniques for industrial waster water.* International Scholarly and Scientific Research & Innovation, 2012. **6**(12): p. 1164-1167.

83. Hensman, C.E., *Removal of Mercury and Other Heavy Metals of Industrial and Contaminated Site Waste Waters by Organic Chelation, Coprecipitation and High-Efficiency Particulate Removal.* United States Environmental Protection Agency, 2001(68D01062).

84. Matlock, M.M., et al., *Aqueous leaching properties and environmental implications of cadmium, lead and zinc Trimercaptotriazine (TMT) compounds.* Water Research, 2001. **35**(15): p. 3649-3655.

85. De Clercq, J., *Removal of mercury from aqueous solutions by adsorption on a new ultra stable mesoporous adsorbent and on a commercial ion exchange resin.* International Journal of Industrial Chemistry, 2012. **3**(1): p. 1.

86. Zganiaris, E., *Ion exchange resins and adsorbents in chemical process.* BOOKS ON DEMAND, 2013. **2nd ed**: p. 53-56.

87. De Clercq, J., *Removal of mercury from aqueous solutions by adsorption on a new ultra stable mesoporous adsorbent and on a commercial ion exchange resin.* International Journal of Industrial Chemistry, 2012. **3**(1): p. 1.

88. XiaoYu Cui, X.H., YongPing Shan, *Study on copper removal from berberine wastewater using ion exchange resin.* Journal of Environment Engineering Technology, 2017. **7**(2): p. 181-187.

Appendix

❖ Chemicals list

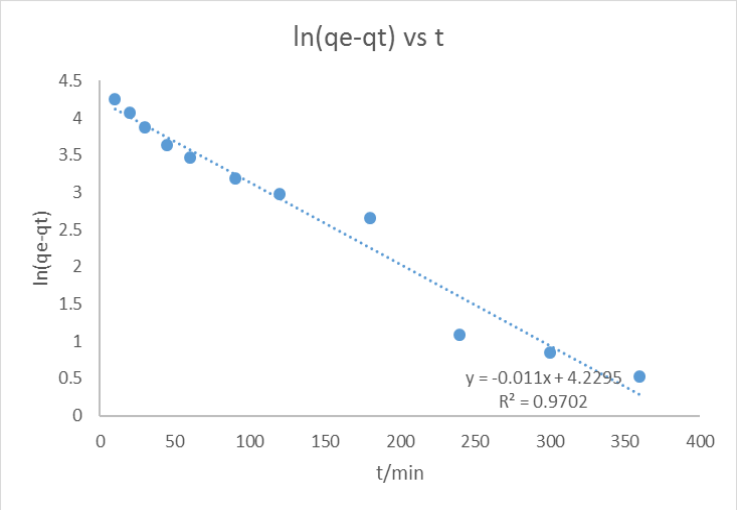
Chemical	Purity	Supplier
Elemental mercury	98%	Sigma-Aldrich
Potassium iodide	99%	Fisher Scientific
Iodine	>98%	Fisher Scientific
Potassium bromide	>99%	Sigma-Aldrich
Sodium bromide	99+%	Sigma-Aldrich
Potassium chloride	>99%	Sigma-Aldrich
Sodium chloride	>99%	Sigma-Aldrich
Hydrochloric acid	>93%	Aldrich
Potassium hydroxide	>98%	Fisher Scientific
TMT-15	98%	Evonik
S924		Purolite
S920		Purolite

❖ Kinetic study of adsorption of Purolite resin

➢ S920

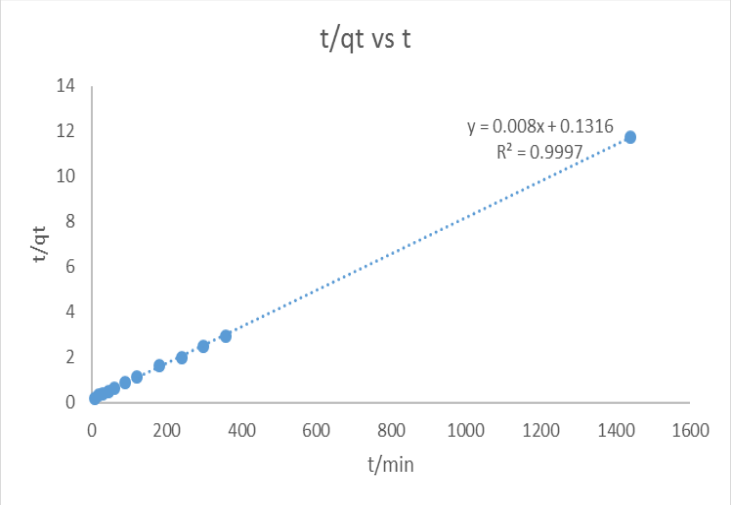
(1) 25 ºC

a) Pseudo-first-order



Equation	
y=-0.011x+4.2295	
$-k_1$=	-0.011
Qe	68.683
R^2	0.9702

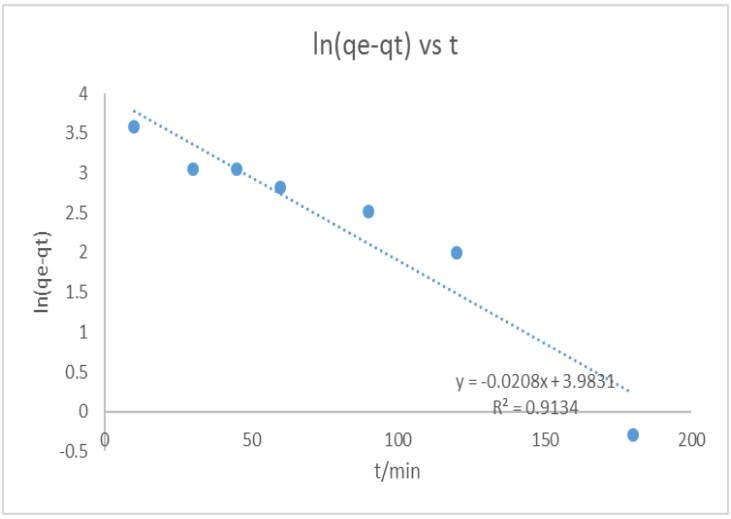
b) Pseudo-second-order



Equation	
y=0.008x+0.1316	
$1/q_e$	0.008
$1/(q_e^2k_2)$	0.1316
qe^2	15625.000
k_2	0.0004863
R^2	0.9997
qe	125

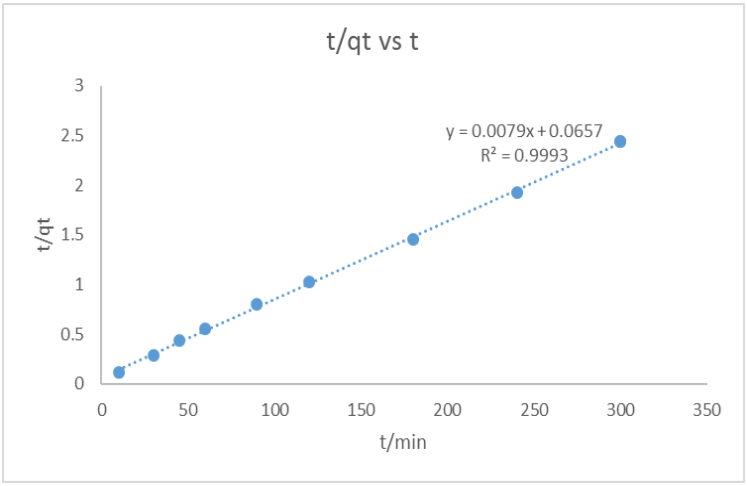
(2) 35 ºC

a) Pseudo-first-order



Equation	
y=-0.0208x+3.9831	
$-k_1$=	-0.0208
Qe	53.68
R^2	0.9134

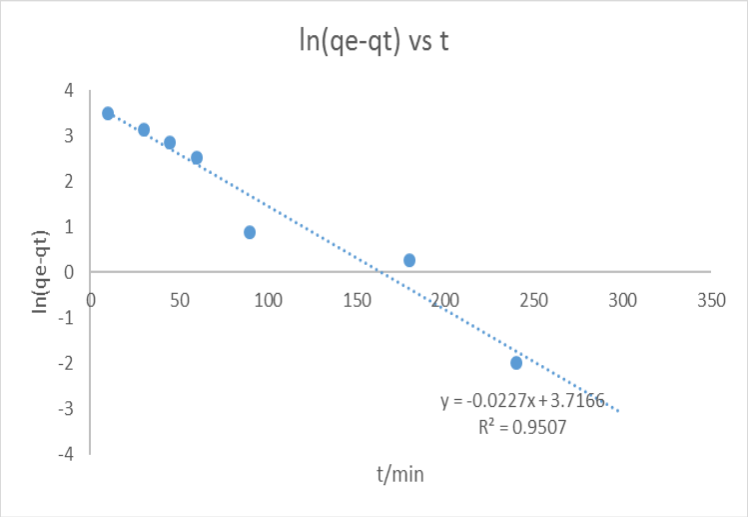
b) Pseudo-second-order



Equation	
y=0.0079x+0.0657	
$1/q_e$	0.0079
$1/(q_e^2k_2)$	0.0657
qe^2	16023.073
k_2	0.0009499
R^2	0.9997
qe	126.58

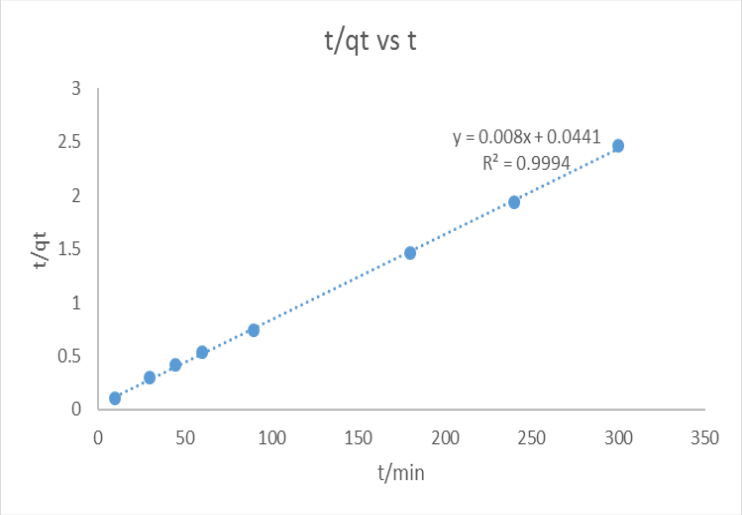
(3) 45 ºC

a) Pseudo-first-order



Equation	
y=-0.0227x+3.7166	
-k1=	-0.0227
Qe	41.12
R2	0.9507

b) Pseudo-second-order

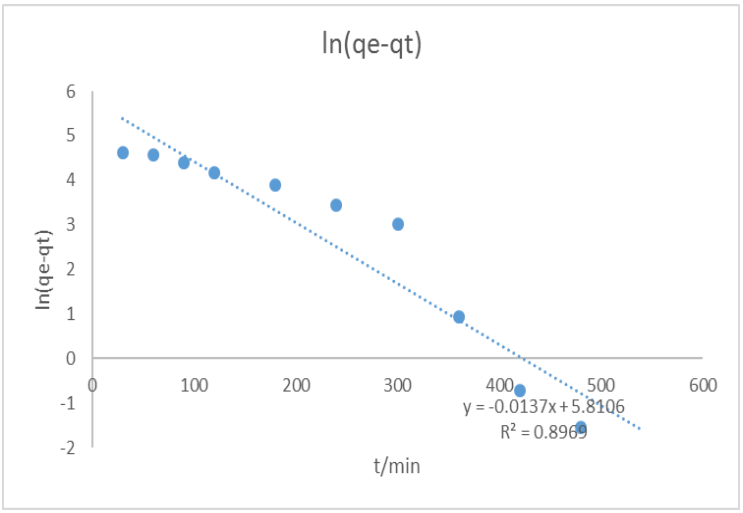


Equation	
y=0.008x+0.0441	
$1/q_e$	0.008
$1/(q_e^2k_2)$	0.0441
qe^2	15625.000
k_2	0.0014512
R^2	0.9997
qe	125

➢ **S924**

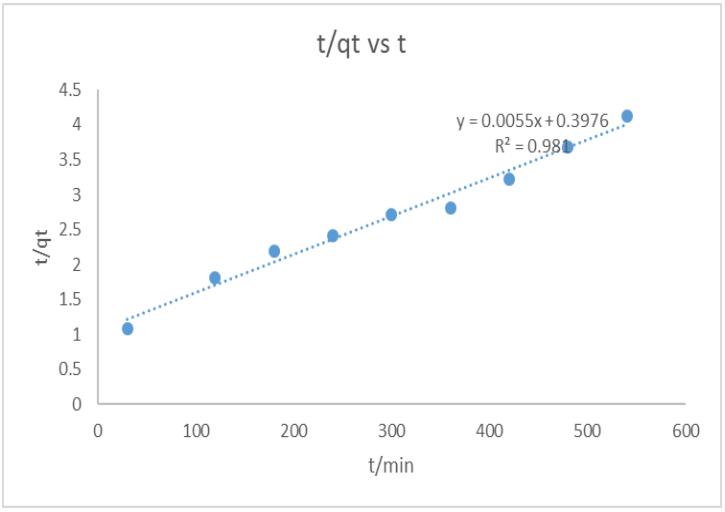
(1) 25 ºC

a) Pseudo-first-order



Equation	
y=-0.0137x+5.8106	
$-k_1$=	-0.0137
Qe	333.82
R^2	0.8969

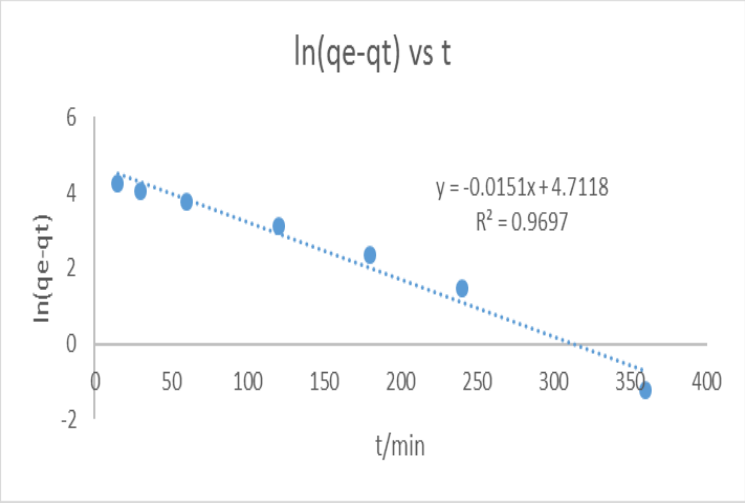
b) Pseudo-second-order



Equation	
y=0.0055x+0.3976	
$1/q_e$	0.0055
$1/(q_e^2k_2)$	0.3976
qe^2	21626.298
k_2	0.0001163
R^2	0.981
qe	147.06

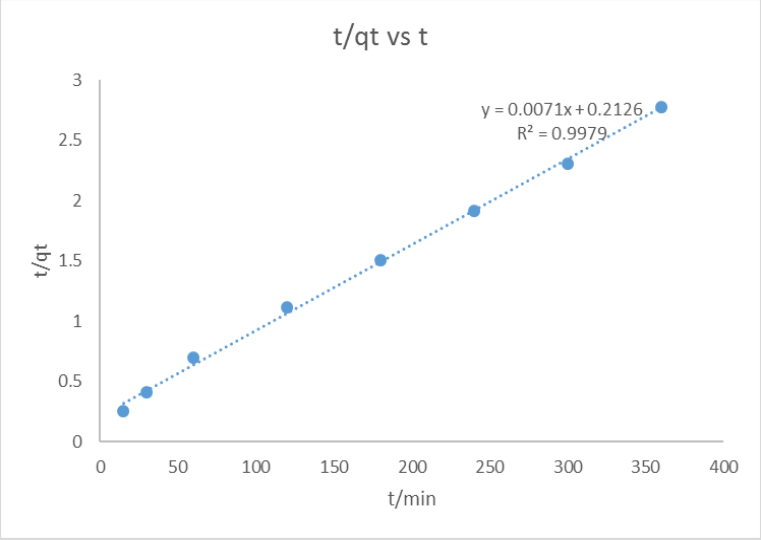
(2) 35 ºC

a) Pseudo-first-order



Equation	
y=-0.0151x+4.7118	
$-k_1$=	-0.0151
Qe	111.25
R^2	0.09697

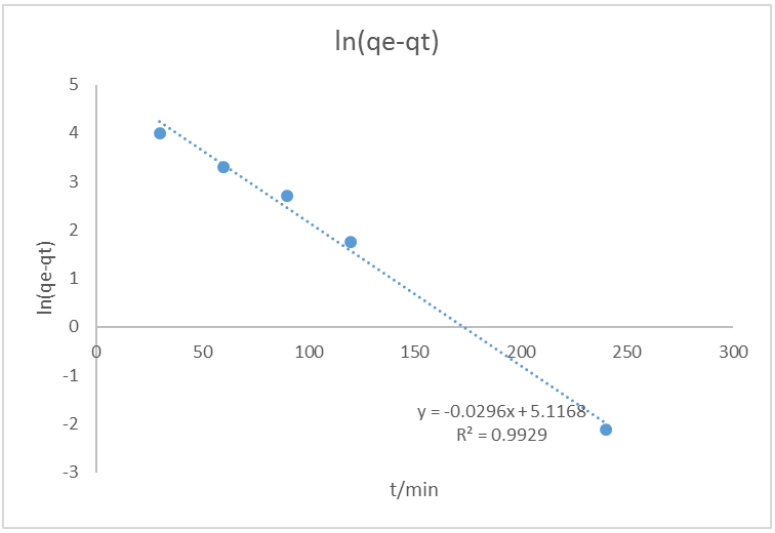
b) Pseudo-second-order



Equation	
y=0.0071x+0.2126	
$1/q_e$	0.0071
$1/(q_e^2k_2)$	0.2126
qe^2	19837.334
k_2	0.0001723
R^2	0.9979
qe	140.85

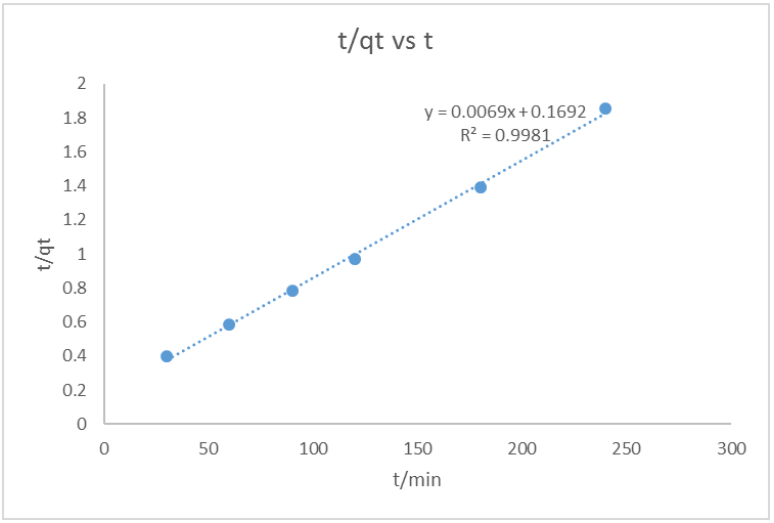
(3) 45 ºC

a) Pseudo-first-order



Equation	
y=-0.0296x+5.1168	
$-k_1$=	-0.0296
Qe	166.80
R^2	0.9929

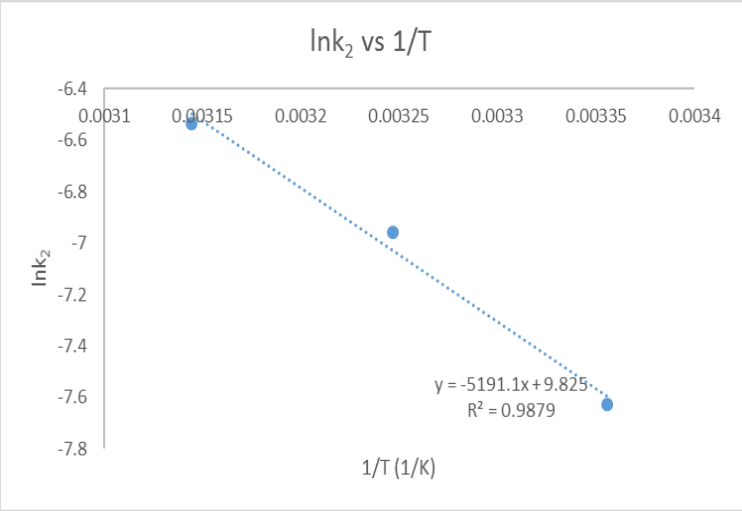
b) Pseudo-second-order



Equation	
y=0.0069x+0.1692	
$1/q_e$	0.0069
$1/(q_e^2k_2)$	0.1692
qe^2	21004.705
k_2	0.0002814
R^2	0.9981
qe	144.93

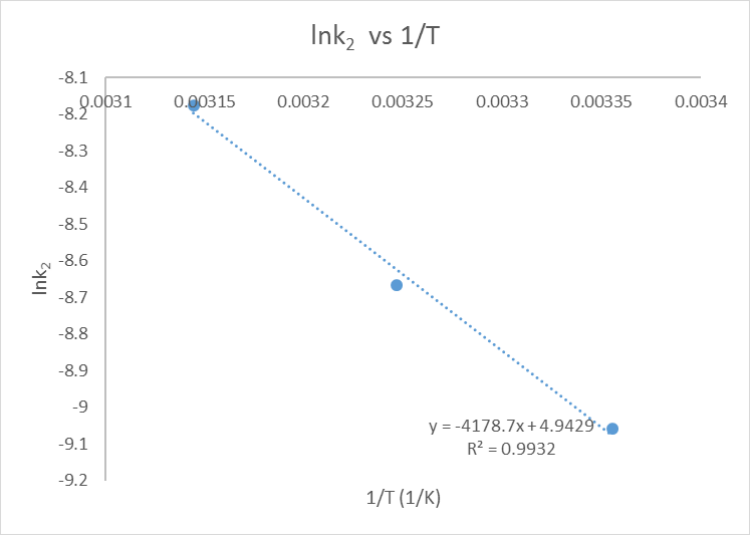
❖ Activation energy (Ea) of adsorption of Purolite resin

(1) S920



pseudo second order y=-519.1x+9.825	
lnk_0	9.825
-Ea/R	-519.1
k_0	18490.27
Ea	4316.057
R^2	0.9879

(2) S924



pseudo second order y=-4178.7x+4.9429	
lnk_0	4.9429
-Ea/R	-4178.8
k_0	140.1762
Ea	34744.63
R^2	0.9932